Improved Fits for the Vibrational and Rotational Constants of Many States of Nitrogen and Oxygen

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All pertinent measurements of the vibrational intervals $\Delta G(v+\frac{1}{2})$ and rotational constants B_v for 11 states of N_2, four states of N_2^+, the ground state of O_2, and four states of O_2^+ that could be found in published papers have been assembled and plotted against v. (These are the states important in modeling the fluorescence produced when air is bombarded by fast electrons.) These values of ΔG and B_v are compared with values calculated from the standard polynomials in powers of $v+\frac{1}{2}$, using the coefficients tabulated by Huber and Herzberg (1979), as well as coefficients derived by later analysts, when available. In about 25 percent of the states considered, the coefficients of Huber and Herzberg are found to still yield good fits to the latest available spectroscopic data. In another 25 percent, good fits are obtained from more recently published coefficients. For the remaining 50 percent of the states, new improved coefficients have been derived by least-squares fitting. The results are tabulated and plotted.

Key words: air fluorescence; critical review; data compilation; molecular nitrogen; molecular oxygen; rotational constants; spectroscopic constants; vibrational constants.

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1. Introduction

In predicting or analyzing the radiation from disturbed or heated air, one often must deal with transitions among excited states of nitrogen and oxygen. In the aurora, for example, energetic charged particles inelastically scatter in the upper atmosphere to produce a myriad of highly excited electronic, vibrational, and rotational states of N_2, N_2^+, O_2, and O_2^+. These excited states can radiatively de-excite by making one or more transitions to successively less energetic states until ultimately the stable ground state is reached. As more sophisticated models are developed which include transitions among excited states with high vibrational levels, molecular constants valid for high vibrational levels are needed to accurately predict the wavelengths of these transitions, and to calculate quantities such as Franck-Condon factors which determine the relative rates of these transitions.

More than a decade has passed since the publication of Huber and Herzberg's book *Constants of Diatomic Molecules* (1979), Lofthus and Krupenie's monograph *The Spectrum of Molecular Nitrogen* (1977), and Krupenie's monograph *The Spectrum of Molecular Oxygen* (1972). These standard works have been extremely useful in many areas of geophysical research, as evidenced by the hundreds of published scientific reports in which references to these works are made. In the past ten years, however, new spectroscopic measurements have become available which affect some of the molecular constants published in these works. Frequently this is because the recent measurements extend to higher vibrational levels than the old ones. For example, Piper *et al.* (1989) pointed out inadequacies in the tabulated constants of Lofthus and Krupenie for the N_2 A and B states at high vibrational levels, and consequently used the constants determined by Roux *et al.* (1983). As another example, James *et al.* (1988) calculated Franck-Condon factors for the O_2^+ A–X band system for vibrational levels v' and $v''=0$ to 25 using the constants of Huber and Herzberg; the new data of Coxon and Haley (1984) make it possible to derive improved constants for these O_2^+ states.

The purpose of this report is to combine the most recent spectroscopic data with the older data in order to derive improved vibrational and rotational constants for several states of N_2, N_2^+, and O_2^+, as well as the ground state of O_2. Only those states that are important in modeling air fluorescence are covered. Some of these states are also important in modeling airglow phenomena; however, not all states involved in the airglow are included in this report, particularly the excited states of O_2. For these the interested reader may refer to an article by Slanger and Cosby (1988), who summarized recent vibrational and rotational data on the six lowest states of O_2.

2. Method of Analysis

In the present work, for each molecular state the available spectroscopic data on vibrational energy intervals $\Delta G(v+\frac{1}{2})$, and rotational constants B_v, were compiled from published papers and plotted separately. In most of these papers vibrational energy intervals were not tabulated, and therefore had to be calculated. The vibrational energy interval is defined by

$$\Delta G(v+\tfrac{1}{2}) \equiv G(v+1) - G(v), \qquad (1)$$

where $G(v)$ is the relative energy of the rotationless vibrational level v. Vibrational energy intervals of the upper (lower) state of a given band system are found by taking the difference between band origins of transitions with common lower (upper) levels, and upper (lower) levels separated by $\Delta v = 1$. In some cases band-head data, although not as accurate as band-origin data, were used to calculate vibrational energy intervals as a means of extending the data to higher vibrational levels. Rotational constants B_v, on the other hand, are generally available from published reports so that derivation of these quantities by analysis of the rotational line positions was not required.

Before plotting $\Delta G(v+\frac{1}{2})$ and B_v, linear terms in v were added to these quantities in order to offset linear variations, so that the smaller nonlinear variations of these quantities with v could be displayed on an expanded plot scale. Thus the quantities $\Delta G(v+\frac{1}{2}) + pv$ and $B_v + qv$ are plotted against v in the figures, where p and q are constant coefficients that are chosen individually for each state.

In addition to the basic data, each graph includes one or more curves calculated from the standard polynomial expressions in $v + \frac{1}{2}$ (see Tables 1–4 for these expressions). In most cases a curve computed using the coefficients (molecular constants) of Huber and Herzberg (1979) is plotted. Curves computed using constants published elsewhere are also plotted when warranted. If none of these curves appears to give an optimum fit to the data now available, a new polynomial fit was made, using the method of least squares. The order of the polynomial was chosen so that the data are adequately represented by a minimum number of coefficients. In order to influence the fit in some cases, the more accurate measurements were given greater weight, and less accurate data were sometimes omitted from the fit entirely. A curve for each new fit is also plotted. By comparing the fits with the data shown in the figures, the general validity of the fits can be easily inferred.

The recommended molecular constants based on these fits are presented in Tables 1 and 2 for nitrogen, and 3 and 4 for oxygen. The symbolic notation of the tabulated constants follows that of Huber and Herzberg (1979) and Lofthus and Krupenie (1977), except for the addition of some higher order terms as defined on the tables. The last column in each table indicates either the reference from which the constants were taken or the fact that they were derived from a new fit. In some references the constants are listed with more precision than justified by the basic data or the quality of the fits. In these cases, the values listed here have been rounded off.

In this report, higher-order terms in the rotational quantum number, such as $D_v J^2 (J+1)^2$, are not considered because in most air fluorescence situations the rotational temperature is low enough that these terms can be neglected. New data on the values of D_v for many of the states are available, however, and may be found in the more recent references cited within this report.

TABLE 1. Vibrational constants (cm^{-1}) of N_2 and N_2^+

$$T_v = T_e + \omega_e (v+\tfrac{1}{2}) - \omega_e x_e (v+\tfrac{1}{2})^2 + \omega_e y_e (v+\tfrac{1}{2})^3 + \omega_e z_e (v+\tfrac{1}{2})^4 + \omega_e a_e (v+\tfrac{1}{2})^5$$
$$T_e = T_0 - \omega_e/2 + \omega_e x_e/4 - \omega_e y_e/8 - \omega_e z_e/16 - \omega_e a_e/32$$

State		T_0*	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$\omega_e a_e$	Source of vibr. consts.
N_2^+	$C\ ^2\Sigma_u^+$	190209.5	2071.5	9.29	−0.43			1
	$B\ ^2\Sigma_u^+$	151233.5	2420.83	23.851	−0.3587	−6.192(−2)†		2
	$A\ ^2\Pi_u$	134683.1	1903.51	15.029	2.03(−3)			2
	$X\ ^2\Sigma_g^+$	125667.5	2207.37	16.302	−2.67(−3)	−2.61(−3)	3.7(−5)	3
N_2	$D\ ^3\Sigma_u^+$	103570.9	(2207)	(16.3)	(−2.7)(−2)	(−2.6)(−3)		3
	$E\ ^3\Sigma_g^+$	95774.5	(2218)	(16.3)	(−2.7)(−2)	(−2.6)(−3)		3
	$C\ ^3\Pi_u$	88977.9	2047.18	28.445	2.0883	−5.350(−1)		1, ‡
	$w\ ^1\Delta_u$	71698.4	1559.50	12.008	4.54(−2)			4
	$a\ ^1\Pi_g$	68951.2	1694.21	13.949	7.94(−3)	2.9(−4)		1
	$a'\ ^1\Sigma_u^-$	67739.3	1530.25	12.075	4.13(−2)	−2.9(−4)		1
	$B'\ ^3\Sigma_u^-$	65851.3	1516.88	12.181	4.19(−2)	−7.3(−4)		1
	$W\ ^3\Delta_u$	59380.2	1506.53	12.575	3.09(−2)	−7.1(−4)		3
	$B\ ^3\Pi_g$	59306.8	1734.38	14.558	1.40(−2)	−1.13(−3)		3
	$A\ ^3\Sigma_u^+$	49754.8	1460.48	13.775	−1.175(−2)	1.41(−4)	−7.29(−5)	3
	$X\ ^1\Sigma_g^+$	0.0	2358.57	14.324	−2.26(−3)	−2.4(−4)		1

*Derived from ν_{00} band origins of Huber and Herzberg (1979) and ionization potentials of Lofthus and Krupenie (1977), except for the N_2 W and B' states which are from Cerny *et al.* (1980) and Roux and Michaud (1988), respectively (see Sec. 2).

†Read as -6.192×10^{-2}.

‡Applicable only to $v = 0-4$.

[1] From Huber and Herzberg (1979).

[2] From Gottscho *et al.* (1979).

[3] From a new fit to the experimental ΔG values (see text and figures).

[4] From Lofthus and Krupenie (1977).

TABLE 2. Rotational constants (cm^{-1}) of N_2 and N_2^+

$$B_v = B_e - \alpha_e (v+\tfrac{1}{2}) + \gamma_e (v+\tfrac{1}{2})^2 + \delta_e (v+\tfrac{1}{2})^3 + \epsilon_e (v+\tfrac{1}{2})^4$$

State		B_e	α_e	γ_e	δ_e	ϵ_e	Source of rot. consts.
N_2^+	$C\ ^2\Sigma_u^+$	1.5114	1.10(−3)*	−8.2(−4)			1
	$B\ ^2\Sigma_u^+$	2.0845	2.132(−2)	−8.5(−4)			2
	$A\ ^2\Pi_u$	1.7442	1.838(−2)	−1.76(−4)	4.4(−6)		1
	$X\ ^2\Sigma_g^+$	1.93177	1.900(−2)	−1.91(−5)	−5.00(−6)	4.6(−8)	1
N_2	$D\ ^3\Sigma_u^+$	1.9705	(1.90)(−2)	(−1.9)(−4)			1
	$E\ ^3\Sigma_g^+$	1.9368	(1.90)(−2)	(−1.9)(−4)			1
	$C\ ^3\Pi_u$	1.8247	1.868(−2)	−2.28(−3)	7.33(−4)	−1.5(−4)	3, †
	$w\ ^1\Delta_u$	1.4963	1.63(−2)				1
	$a\ ^1\Pi_g$	1.6169	1.793(−2)	−2.93(−5)			3
	$a'\ ^1\Sigma_u^-$	1.4799	1.657(−2)	2.41(−5)			3
	$B'\ ^3\Sigma_u^-$	1.4731	1.668(−2)	1.84(−5)	−4.5(−7)		1
	$W\ ^3\Delta_u$	1.47021	1.6997(−2)	−1.01(−5)	3.3(−7)		1
	$B\ ^3\Pi_g$	1.63802	1.8302(−2)	−8.4(−6)	−3.4(−6)		1
	$A\ ^3\Sigma_u^+$	1.45499	1.8385(−2)	1.24(−5)	−6.7(−6)		1
	$X\ ^1\Sigma_g^+$	1.99824	1.7318(−2)	−3.3(−5)			3

*Read as 1.10×10^{-3}.

†Applicable only to $v=0-4$.

[1] From a new fit to the experimental B_v values (see text and figures).

[2] From Gottscho *et al.* (1979).

[3] From Huber and Herzberg (1979).

TABLE 3. Vibrational constants (cm^{-1}) of O_2 and O_2^+

$$T_v = T_e + \omega_e (v+\tfrac{1}{2}) - \omega_e x_e (v+\tfrac{1}{2})^2 + \omega_e y_e (v+\tfrac{1}{2})^3 + \omega_e z_e (v+\tfrac{1}{2})^4 + \omega_e a_e (v+\tfrac{1}{2})^5 + \omega_e b_e (v+\tfrac{1}{2})^6$$
$$T_e = T_0 - \omega_e /2 + \omega_e x_e / 4 - \omega_e y_e / 8 - \omega_e z_e / 16 - \omega_e a_e /32 - \omega_e b_e / 64$$

State		T_0*	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$\omega_e a_e$	$\omega_e b_e$	Source of vibr. consts.
O_2^+	$b\ ^4\Sigma_g^-$	146556	1197.02	17.172	1.18(−2)†	−1.0(−3)			1
	$A\ ^2\Pi_u$	137433.1	899.00	13.726	1.00(−2)				2
	$a\ ^4\Pi_u$	129889.3	1035.13	10.115	−3.31(−2)	2.1(−4)			2
	$X\ ^2\Pi_g$	97365	1906.07	16.512	2.11(−2)	−7.1(−4)			3
O_2	$X\ ^3\Sigma_g^-$	0.0	1580.39	12.112	7.54(−2)	−4.09(−3)	1.30(−4)	−2.21(−6)	2

*Derived from ν_{00} band origins of Huber and Herzberg (1979) and ionization potentials of Krupenie (1972).

†Read as 1.18×10^{-2}.

[1] From Hansen *et al.* (1983).

[2] From a new fit to the experimental ΔG values (see text and figures).

[3] From Coxon and Haley (1984), after correcting the power of ten of $\omega_e z_e$.

Tables 1 and 3 include columns for T_0, which is the energy of an excited or ionic state relative to the $v=0$, $J=0$ level of the corresponding neutral ground state. T_0 is tabulated, rather than the equilibrium term value T_e, since T_0 is directly measured and does not depend on the choice of vibrational constants ω_e, etc. The formula which relates T_0 to T_e is given on the tables. For most of the states, T_0 is derived from the ν_{00} band origins tabulated by Huber and Herzberg (1979), with the following exceptions: For the N_2 W state, T_0 is the sum of the term value of Cerny *et al.* (1980) for the W state relative to the A state and ν_{00} of Huber and Herzberg for the A–X transition. For the N_2 B' state, T_0 is the sum of ν_{00} of Roux and Michaud (1988) for the B'–B transition and ν_{00} of Huber and Herzberg for the B–X transition. The new values of T_0 for the N_2 W and B' states are within 1 cm^{-1} of the values of Huber and Herzberg.

3. Results for Nitrogen

3.1. N_2 $X\ ^1\Sigma_g^+$

In Fig. 1 vibrational data for the $X\ ^1\Sigma_g^+$ state of N_2 from several investigations are plotted together with a curve computed using the constants listed by Huber and Herzberg (1979). The Huber and Herzberg curve agrees

TABLE 4. Rotational constants (cm^{-1}) of O_2 and O_2^+

$$B_v = B_e - \alpha_e (v+\tfrac{1}{2}) + \gamma_e (v+\tfrac{1}{2})^2 + \delta_e (v+\tfrac{1}{2})^3 + \epsilon_e (v+\tfrac{1}{2})^4$$

State		B_e	α_e	γ_e	δ_e	ϵ_e	Source of rot. consts.
O_2^+	$b\ ^4\Sigma_g^-$	1.28766	2.192(−2)*	−1.28(−4)			1
	$A\ ^2\Pi_u$	1.0617	1.941(−2)	−1.27(−4)			2
	$a\ ^4\Pi_u$	1.10476	1.548(−2)	1.2(−5)	−5.0(−6)		3
	$X\ ^2\Pi_g$	1.6896	1.930(−2)	−1.9(−5)	−1.6(−6)		4
O_2	$X\ ^3\Sigma_g^-$	1.4451	1.523(−2)	−8.25(−5)	7.25(−6)	−2.09(−7)	2

*Read as 2.192×10^{-2}.

[1] From Hansen *et al.* (1983).

[2] From a new fit to the experimental B_v values (see text and figures).

[3] From Hansen *et al.* (1983), after correcting the γ_e value (see text).

[4] From Coxon and Haley (1984), after correcting the sign of δ_e.

well with the best data below $v = 16$, and reasonably well with the scattered data at higher v, so a new fit is not required. Accordingly, the vibrational constants of Huber and Herzberg are given in Table 1.

Figure 2 shows rotational data for the $X\ ^1\Sigma_g^+$ state of N_2 from various sources. Similar, additional data not given in the figure are measurements of B_0 by Stoicheff (1954), Lofthus (1960), Vanderslice *et al.* (1965), and Butcher *et al.* (1971); less accurate measurements of B_v for $v = 0$ through 14 may be found in Watson and Koontz (1934) and Spinks (1942). The figure shows that the curve computed using the constants given by Huber and Herzberg (1979) fits the available data very well, so these constants are listed in Table 2.

3.2. N_2 $A\ ^3\Sigma_u^+$

The vibrational data of Dieke and Heath (1959), Tanaka and Jursa (1961), Roux *et al.* (1983), and Verma (1984) for the $A\ ^3\Sigma_u^+$ state of N_2 are plotted in Fig. 3. The more recent data are not substantially different from the older data, although their accuracy appears to be higher. Curves computed using the constants of Huber and Herzberg (1979) and of Roux *et al.* are also given in Fig. 3. The constants of Huber and Herzberg are from Lofthus and Krupenie (1977) (except for a sign error in $\omega_e y_e$ in Lofthus and Krupenie's tabulation), and are based on the data of Dieke and Heath. The constants of Roux *et al.* are based only on their own measurements which do not go to vibrational levels as high as do Dieke and Heath's measurements. Both of these curves lie significantly above the band-head data of Tanaka and Jursa for $v > 13$, so we have made a new fit, shown by the solid curve. The corresponding new constants are listed in Table 1.

In Fig. 4, various rotational data and three different fits are plotted for the $A\ ^3\Sigma_u^+$ state of N_2. The constants of Huber and Herzberg (1979) are from Lofthus and Krupenie (1977) which are based on the data of Miller (1966) and Dieke and Heath (1959). Again, the constants of Roux *et al.* (1983) are based only on their own measurements. Both of these published fits deviate from the recent measurements at higher v by Verma (1984), so we have made the new fit shown in the figure and listed in Table 2. [Since the recent measurements of Carroll and Croke (1989) are apparently not as accurate as Verma's, they were not included in the new fit.]

3.3. N_2 $B\ ^3\Pi_g$

The vibrational data of Dieke and Heath (1959), Roux *et al.* (1983), Verma (1984), and Roux and Michaud (1988) for the $B\ ^3\Pi_g$ state of N_2 are shown in Fig. 5. The oldest of these measurements covers the largest number of vibrational levels. The constants of Huber and Herzberg (1979) are from Lofthus and Krupenie (1977); apparently these contain an error which is not a simple typographical one. The fits of Cerny *et al.* (1980) and Roux *et al.* are based on their own high precision measurements which do not cover as many vibrational levels as Dieke and Heath. To better represent the latter data at $v = 14-16$, we have made the new fit shown by the solid curve.

The B_v measurements of Dieke and Heath (1959), Roux *et al.* (1983), Verma (1984), and Carroll and Croke (1989) for the $B\ ^3\Pi_g$ state of N_2 are plotted in Fig. 6. Other measurements not shown in the figure may be found in Budo (1937), Carroll (1952), and Carroll (1963) for $v = 3$, 4, and 11. The new fit, which is based on the data plotted in Fig. 6 except for the less accurate measurement of Carroll and Croke, differs from the fits of Huber and Herzberg (1979) and Roux *et al.* in order to better represent the recent measurements of Verma for $v > 11$.

3.4. N_2 $W\,^3\Delta_u$

In Figs. 7 and 8 the vibrational and rotational data of Cerny *et al.* (1980) and Roux and Michaud (1988) are plotted along with several fits. The linear curve in Fig. 7 is based on the vibrational constants tabulated by Huber and Herzberg (1979), which were derived by Benesch and Saum (1971) from approximate band origins. No rotational data were available until 1980, when Cerny *et al.* measured N_2 W–B band origins and rotational structure for $v' \leq 7$, and derived constants based on these data. In later work Roux and Michaud extended the data base to $v'=12$ and provided updated constants; however, in the course of the present work it was discovered that the values in their Table VIII do not fit their data for $G(v)$ and B_v. Therefore updated values, based on the new fits of the data shown in Figs. 7 and 8, are listed in Tables 1 and 2.

3.5. N_2 $B'\,^3\Sigma_u^-$

The vibrational and rotational data for the $B'\,^3\Sigma_u^-$ state of N_2 from several investigations are plotted in Figs. 9 and 10, along with curves calculated from the constants given by Huber and Herzberg (1979), which are from Lofthus and Krupenie (1977), and from constants given by Roux and Michaud (1988), which are based on their own measurements but do not cover vibrational levels as high as do the measurements of Tilford *et al.* (1965b). As seen in Fig. 9, the vibrational constants of Huber and Herzberg give practically as good fits for $v \leq 12$ as the constants of Roux and Michaud, and much better for $v > 12$. Accordingly, the former are recommended. For the rotational data, neither published set of constants gives a good fit for the entire range of v, so a new fit was made, using just the accurate data of Roux and Michaud for $v \leq 9$ and, with less weight, the Tilford data for $v > 12$.

3.6. N_2 $a'\,^1\Sigma_u^-$

The available vibrational and rotational for this state are plotted in Figs. 11 and 12, along with curves computed using the constants of Huber and Herzberg (1979). It is seen that the curves fit the data adequately. These constants are therefore recommended, and listed in Tables 1 and 2.

3.7. N_2 $a\,^1\Pi_g$

Figures 13 and 14 show the relevant data for the $a\,^1\Pi_g$ state of N_2. Since the constants of Huber and Herzberg (1979) yield curves that fit the best available data satisfactorily, they are recommended and listed in the tables.

3.8. N_2 $w\,^1\Delta_u$

Figure 15 shows the available vibrational data for the $w\,^1\Delta_u$ state of N_2, along with the fits of Huber and Herzberg (1979) and Lofthus and Krupenie (1977). The constants of Lofthus and Krupenie fit the band-origin data more accurately than the linear expression of Huber and Herzberg, which was based on older, less-accurate band-head data, so the Lofthus and Krupenie constants are listed in Table 1.

Rotational data and fits for this state are shown in Fig. 16. Since the fit of Huber and Herzberg (1979) differs significantly from the newer data of Roux *et al.* (1982), a new fit was made, as shown, and the new constants listed in Table 2.

3.9. N_2 $C\,^3\Pi_u$

Dieke and Heath (1959) reported vibrational data for the $C\,^3\Pi_u$ state of N_2 for $v = 0-4$ and derived vibrational constants. Tilford *et al.* (1965c) later determined band origins for the $C\,^3\Pi_u$–$X\,^1\Sigma_g^+$ 0–0, 1–0, and 2–0 bands. In addition they made slight revisions to the vibrational data of Dieke and Heath as a result of their analysis. Using these data they then determined new vibrational constants; Huber and Herzberg (1979) included these updated constants in their tabulation. Figure 17 verifies that the curve computed using these constants is in good agreement with the data, and therefore these constants are included in Table 1.

Dieke and Heath (1959) also reported B_v values for $v=0-4$ for this state, and used these data to derive rotational constants. Tilford *et al.* (1965c) found good agreement between their own measurements of B_v and those of Dieke and Heath. The constants of Dieke and Heath are included in the tabulation of Huber and Herzberg (1979). Figure 18 shows that the curve computed using these constants is in good agreement with the data, and therefore these constants are included in Table 2. It should be noted that these tabulated vibrational and rotational constants must not be used to extrapolate to higher levels, since the so-called C ($v=5$) level contains an admixture of the $C'\,^3\Pi_u$ state, and no bound levels corresponding to $v>5$ exist (see Ledbetter and Dressler, 1976).

3.10. N_2 $E\,^3\Sigma_g^+$

Only transitions from the $E\,^3\Sigma_g^+$ state of N_2 with $v'=0$ and 1 have been observed in emission studies (Herman, 1945; Freund, 1969), which indicates that predissociation probably occurs for the higher vibrational levels (Lofthus and Krupenie, 1977); no absorption study of this state has been carried out. From the rotational structure of the $E\,^3\Sigma_g^+$ state, Carroll and Doheny (1974) determined $B_0 = 1.9273$ cm^{-1}. Thus, spectroscopic data only for $v=0$ and 1 of this state are available. Since the $E\,^3\Sigma_g^+$ state of N_2 is the first member of a Rydberg series which converges to N_2^+ $X\,^2\Sigma_g^+$ (Lefebvre-Brion and Moser, 1965), it is assumed here that the variation of ΔG and B_v with vibrational level is the same as for N_2^+ $X\,^2\Sigma_g^+$ (which is discussed in Sec. 3.12). The consequent approximate vibrational and rotational constants are listed in parentheses in Tables 1 and 2, respectively.

3.11. N_2 D $^3\Sigma_u^+$

No ΔG data for this state are available since only the $v=0$ level of the D $^3\Sigma_u^+$ state of N_2 has been observed. From rotational analysis Gero and Schmid (1940) obtained a value of $B_0=1.961$ cm^{-1}. This value is tabulated in both Huber and Herzberg (1979) and Lofthus and Krupenie (1977).

The D $^3\Sigma_u^+$ state of N_2, like the E $^3\Sigma_g^+$ state discussed above, is also the first member of a Rydberg series which converges to N_2^+ X $^2\Sigma_g^+$ (Lefebvre-Brion and Moser, 1965). Thus, in the same way as was done in Sec. 3.10, it is assumed for this state that the variation of ΔG and B_v with vibrational level is the same as for N_2^+ X $^2\Sigma_g^+$. The consequent approximate vibrational and rotational constants are listed in parentheses in Tables 1 and 2, respectively.

3.12. N_2^+ X $^2\Sigma_g^+$

Vibrational data from several investigations of the X $^2\Sigma_g^+$ state of N_2^+ are available for $v=0-36$, and are plotted in Fig. 19. The ΔG values of Colbourn and Douglas (1977) and Benesch *et al.* (1980) for $v=0-1$ are not shown in the figure because they are very close to those of Klynning and Pages (1972). Curves calculated using the constants of Huber and Herzberg (1979) and Gottscho *et al.* (1979), as well as a new fit of the data, are also plotted in the figure. The new fit deviates significantly from the previous fits above $v=10$, as can be seen in the figure. The new vibrational constants for this state are listed in Table 1.

Figure 20 shows the available rotational data for this state, except for some redundant data. Also shown are the fits of Huber and Herzberg (1979) and Gottscho *et al.* (1979). Since these fits lie considerably above the data for high v, a new fit was made, as shown by the solid curve, with corresponding coefficients listed in Table 2.

3.13. N_2^+ A $^2\Pi_u$

The available vibrational data for this state are displayed in Fig. 21, along with fits from Huber and Herzberg (1979) and Gottscho *et al.* (1979). The experimental values above $v=4$ are approximate and scattered, because they are determined either from band-head measurements (corrected approximately for the differences between band heads and band origins), or from perturbations in the N_2^+ B state. [The scatter of the points shown in the figure is apparently not due to the interactions with the B state, because the consequent perturbations are generally appreciable only for the higher rotational levels of a few vibrational levels; see Janin *et al.* (1959) and Gottscho *et al.* (1979).] The two fits lie relatively close together, but the fit of Gottscho *et al.* is preferable because it is based on "deperturbed" values for $v=10-17$ and also it fits the $v=0-4$ data more precisely. Accordingly, its coefficients are listed in Table 1.

Figure 22 compares the rotational data for this state with curves representing three fits. This linear fit of Huber and Herzberg (1979) is based just on the B_2 and B_3 values of Colbourn and Douglas (1977); it lies considerably above the data for higher v. The "deperturbed" fit of Gottscho *et al.* (1979) deviates seriously from most of the data points for unknown reasons. This discrepancy cannot be due to the deperturbation, because the discrepancy is large for the $v=0-2$ levels, which are not perturbed because they lie considerably below the lowest level of the B state. Accordingly, a new fit to all the data was made, as shown, and its coefficients are included in Table 2.

3.14. N_2^+ B $^2\Sigma_u^+$

Vibrational and rotational data for the B $^2\Sigma_u^+$ state of N_2^+ are available to quite high vibrational levels, as shown in Figs. 23 and 24. The variation of ΔG and B_v with v is unusual, due to the interaction of this state with the C $^2\Sigma_u^+$ state (see Lofthus and Krupenie, 1977, p. 165). Huber and Herzberg (1979) and Gottscho *et al.* (1979) list vibrational constants which fit the data very well for $v=0-9$ but deviate rapidly for higher v. We tried to fit the data over a larger range of v using a higher-order polynomial, but the fit was not accurate enough for most purposes. Consequently, the constants of Gottscho *et al.* are recommended and listed in Table 1. A similar situation holds for the rotational constants (Fig. 24), except that Gottscho's fit is accurate only for $v=0-5$.

3.15. N_2^+ C $^2\Sigma_u^+$

Vibrational data for this state are shown in Fig. 25. For $v>10$, only the approximate photoelectron values of Asbrink and Fridh (1974) are available. The constants of Huber and Herzberg (1979) are seen to adequately fit the data, so these constants are listed in Table 1.

Figure 26 shows the rotational data of Setlow (1948), Wilkinson (1956), and Carroll (1959) for this state. These data extend only up to $v=6$. No curve for Huber and Herzberg (1979) is plotted since they just list the B_0 of Carroll in their table. The new fit shown in the figure is a least-squares's fit to the values of Carroll, omitting the older, less accurate data. As noted by Carroll, it is not possible to derive a plausible curve that fits both B_0 and B_1 accurately. The least-squares fit adopted here lies close to B_0 and very close to B_v for $v=0-2$, but somewhat below B_1.

4. Results for Oxygen

4.1. O_2 $X\ ^3\Sigma_g^-$

Albritton *et al.*, in work never published but with results quoted in Krupenie (1972), studied the pertinent spectroscopic data available in 1971 and determined the best values for $G(v)$ up to $v=21$. The corresponding ΔG values are plotted in Fig. 27. At about the same time Snopko (1970) made new spectroscopic measurements for $v=3-7$ and obtained ΔG values that agree very well with those of Albritton *et al.* (see Fig. 27). Later, an extensive set of measurements was made by Creek and Nicholls (1975), from which they derived $G(v)$ values up to $v=28$. As shown in Fig. 27, a majority of their values agree quite well with older values. However, several of their values between $v=6$ and 17 deviate significantly, and do not follow a smooth curve, as first noted by Copeland *et al.* (1987). Copeland *et al.* also obtained new spectroscopic data for $v=9-11$ which disagree with the deviant values of Creek and Nicholls, and generally agree with the older data. Above $v=21$ the only available ΔG data are the values of Creek and Nicholls, and a few old approximate values from Herman *et al.* (1961). In this region the Creek and Nicholls values are probably fairly accurate, because they follow a smooth curve and tend to be supported by the approximate values of Herman *et al.*

Albritton *et al.* also derived vibrational constants from the data for $v=0-21$; these constants are reproduced in Krupenie (1972) and Huber and Herzberg (1979). The resulting ΔG curve is plotted in Fig. 27. For $v > 20$ it deviates significantly from the more recent values of Creek and Nicholls (1975). Consequently, we have made a new least-squares fit, including all of the data shown in Fig. 27 except the deviant Creek and Nicholls values at $v=6$, 10, and 12, and the approximate values of Herman *et al.* (1961). The resultant curve is shown in Fig. 27, and the constants listed in Table 3.

Krupenie (1972) has tabulated B_v values derived by a variety of investigators. These values are plotted in Fig. 28, along with values from Herman *et al.* (1961), Snopko (1970), Creek and Nicholls (1975), and Copeland *et al.* (1987). The results of Snopko lie significantly below the other results, for unknown reasons. The results of the older investigations are scattered around the relatively smooth curve followed by the values of Creek and Nicholls.

Rotational constants for this state have been tabulated by Krupenie (1972) and by Huber and Herzberg (1979), based on an unpublished analysis by Albritton *et al.* The corresponding curve, shown in Fig. 28, fits the new data of Creek and Nicholls (1975) fairly well up to $v=14$, but deviates significantly for higher v. Consequently, we have made a new least-squares fit of the Creek and Nicholls values (except the discordant point at $v=5$) and two of the values of Copeland *et al.* (1987), omitting $v=11$. This new fit is shown in Fig. 28, and the corresponding constants listed in Table 4.

4.2. O_2^+ $X\ ^2\Pi_g$

Until the recent work of Coxon and Haley (1984), few accurate spectroscopic data on this state were available. Figures 29 and 30 depict ΔG and B_v values obtained from the Coxon and Haley analysis, as well as curves calculated from the spectroscopic constants that they derived (after correcting obvious power-of-ten and sign errors in their printed values for $\omega_e z_e$ and δ_e, respectively). The curves are seen to fit the basic data quite well, so the corresponding constants are listed in Tables 3 and 4. For comparison, linear curves calculated from the constants listed by Huber and Herzberg (1979) are also shown. These constants are based on older spectroscopic data, and do not yield very good fits to the newer data.

4.3. O_2^+ $a\ ^4\Pi_u$

In Fig. 31 band origin data from several sources are plotted. In addition, curves computed using the vibrational constants of Huber and Herzberg (1979) and Hansen *et al.* (1983) are given, after correcting the published $\omega_e a_e$ value of Hansen *et al.* by a factor of 10 (P. C. Cosby, private communication, 1990). The curve of Hansen *et al.* fits the available data well; however, it gives ΔG values which unrealistically diverge for large v. To avoid this problem, a new fit was made (see Fig. 31), and the corresponding vibrational constants are listed in Table 3.

Rotational data and fits from several reports are plotted in Fig. 32 for this state. The recent, more accurate measurements of Hansen *et al.* (1983) extend the data base up to $v=7$. The rotational constants that they deduced by fitting the data are given in Table 4. Note that their γ_e value has been corrected by a factor of 10 (P. C. Cosby, private communication, 1990).

4.4. O_2^+ $A\ ^2\Pi_u$

The basic vibrational and rotational data for this state, as well as curves computed using the molecular constants of Huber and Herzberg (1979), are plotted in Figs. 33 and 34. Also shown is a curve corresponding to the rotational constants of Coxon and Haley (1984). Since none of the curves give good fits to the newer data for high v levels, we have made least-squares fits to all of the data points shown, except the band-head data and the anomalous B_1 value of Coxon and Haley. The resulting curves are shown in the figures and the corresponding constants listed in Tables 3 and 4.

4.5. O_2^+ $b\ ^4\Sigma_g^-$

In Fig. 35, band-origin data from Krupenie (1972), Cosby *et al.* (1980), Hansen *et al.* (1981), and Hansen *et al.* (1983) are plotted for the $b\ ^4\Sigma_g^-$ state of O_2^+. In addition, curves computed using the vibrational constants of Huber and Herzberg (1979) and Hansen *et al.* (1983) are plotted. The fit of Huber and Herzberg was originally derived from data for $v \leq 3$ by Albritton *et al.* (unpublished), and tabulated in Krupenie (1972). The curve based on the constants of Hansen *et al.* (1983) fits the data for $v \leq 5$ best. The deviant data of Hansen *et al.* (1981) for $v = 6$ and 7 are probably less accurate. Accordingly, the vibrational constants of Hansen *et al.* (1983) are listed in Table 3.

The available rotational data for the $b\ ^4\Sigma_g^-$ state of O_2^+, from Nevin (1940), LeBlanc (1963), Cosby *et al.* (1980), and Hansen *et al.* (1983), are plotted in Fig. 36. In addition, curves computed using the constants of Huber and Herzberg (1979) and of Hansen *et al.* (1983) are plotted in Fig. 36 for comparison. The newer measurements are significantly more accurate than those of LeBlanc which do not fall on the plotted curves. The rotational constants of Hansen *et al.* appear preferable and are listed in Table 4.

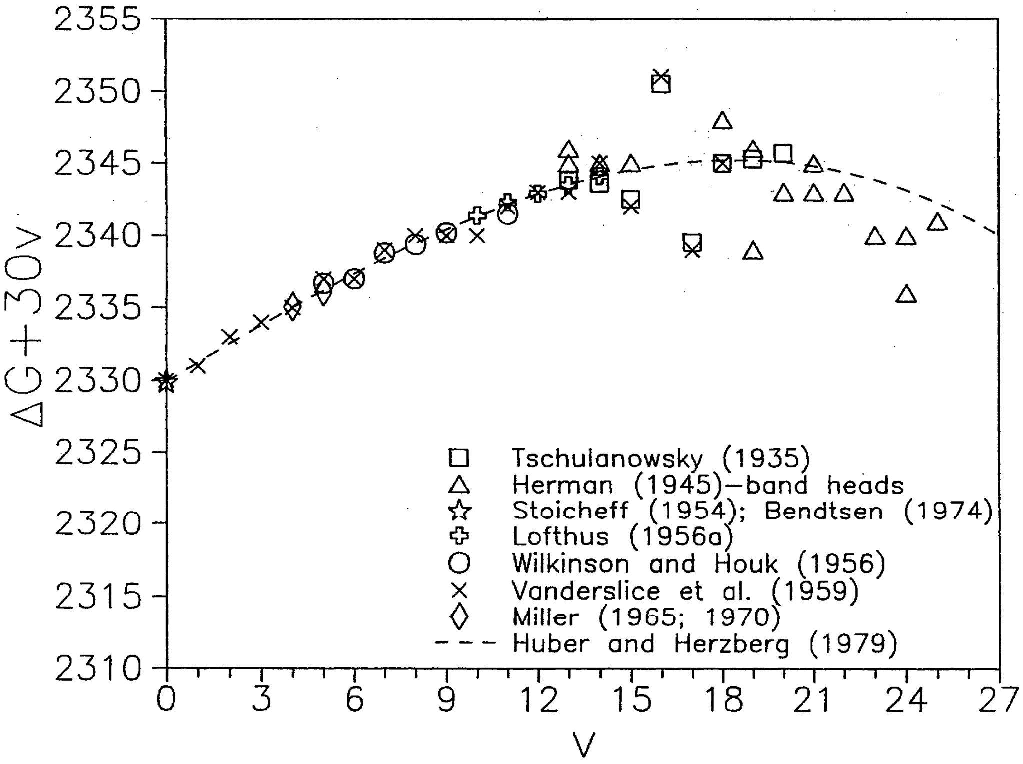

FIG. 1. Vibrational data and fit for the $X\,^1\Sigma_g^+$ state of N_2.

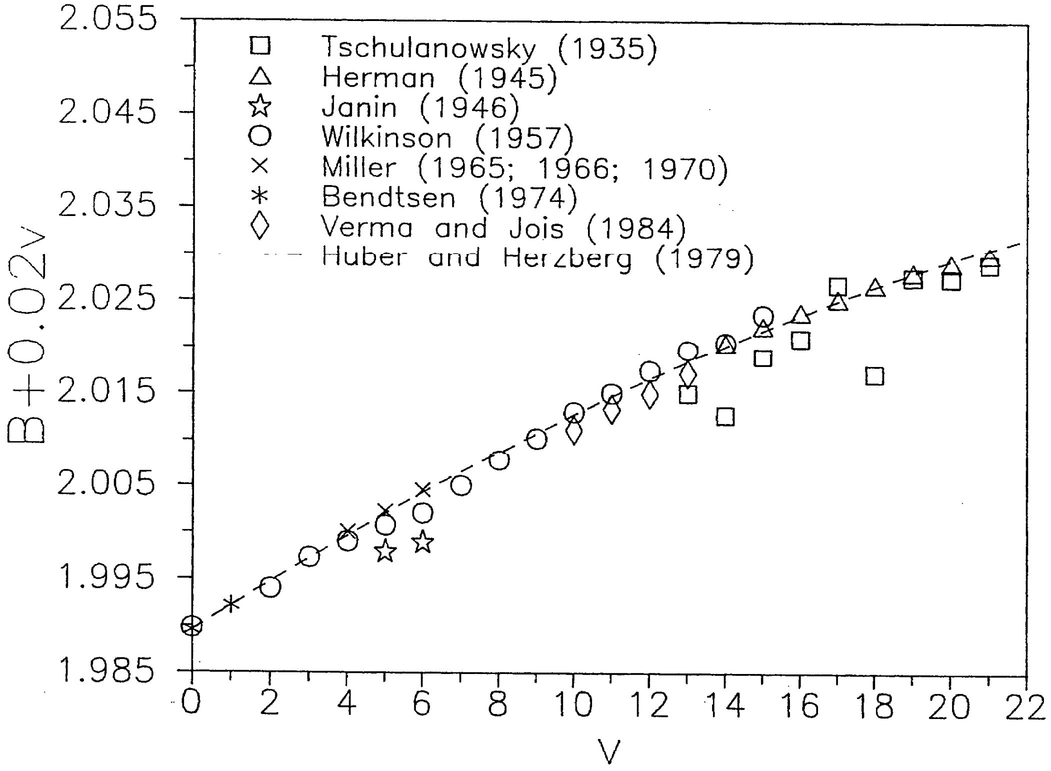

FIG. 2. Rotational data and fit for the $X\,^1\Sigma_g^+$ state of N_2.

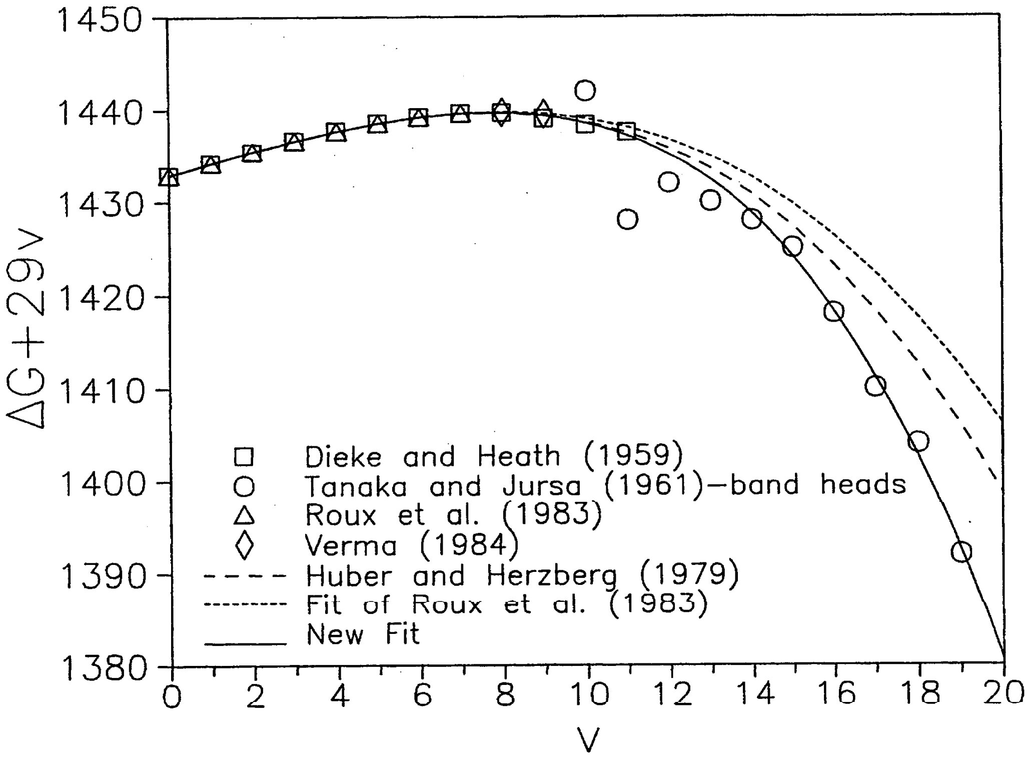

FIG. 3. Vibrational data and fits for the $A\ ^3\Sigma_u^+$ state of N_2.

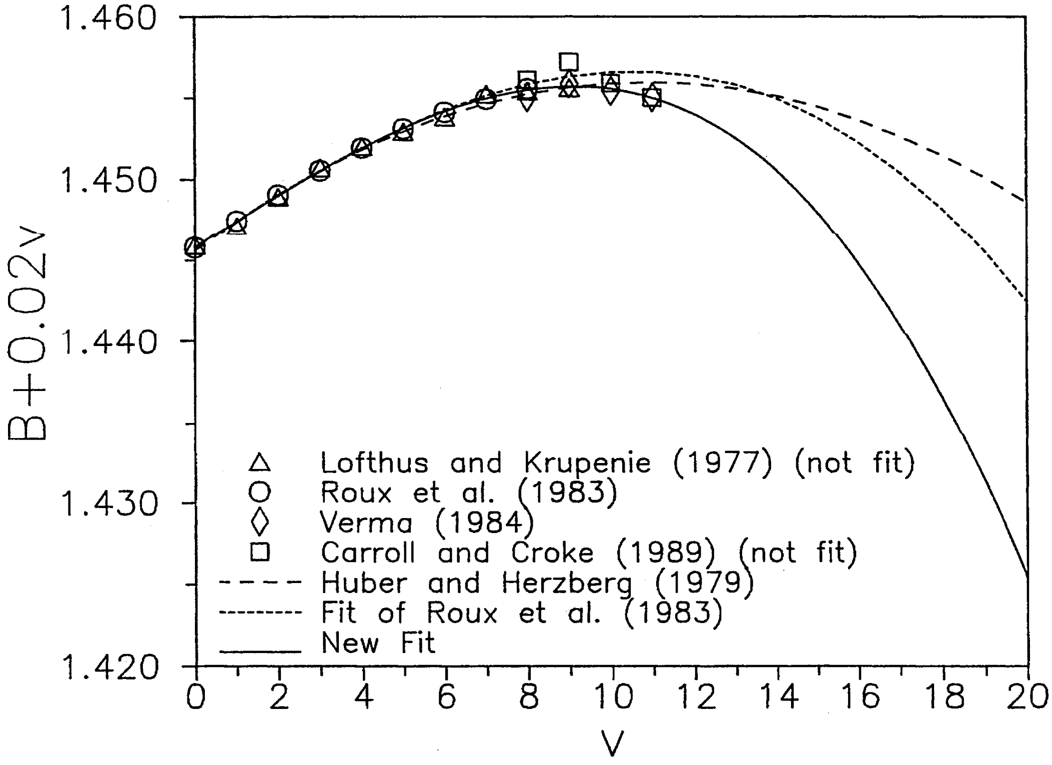

FIG. 4. Rotational data and fits for the $A\ ^3\Sigma_u^+$ state of N_2.

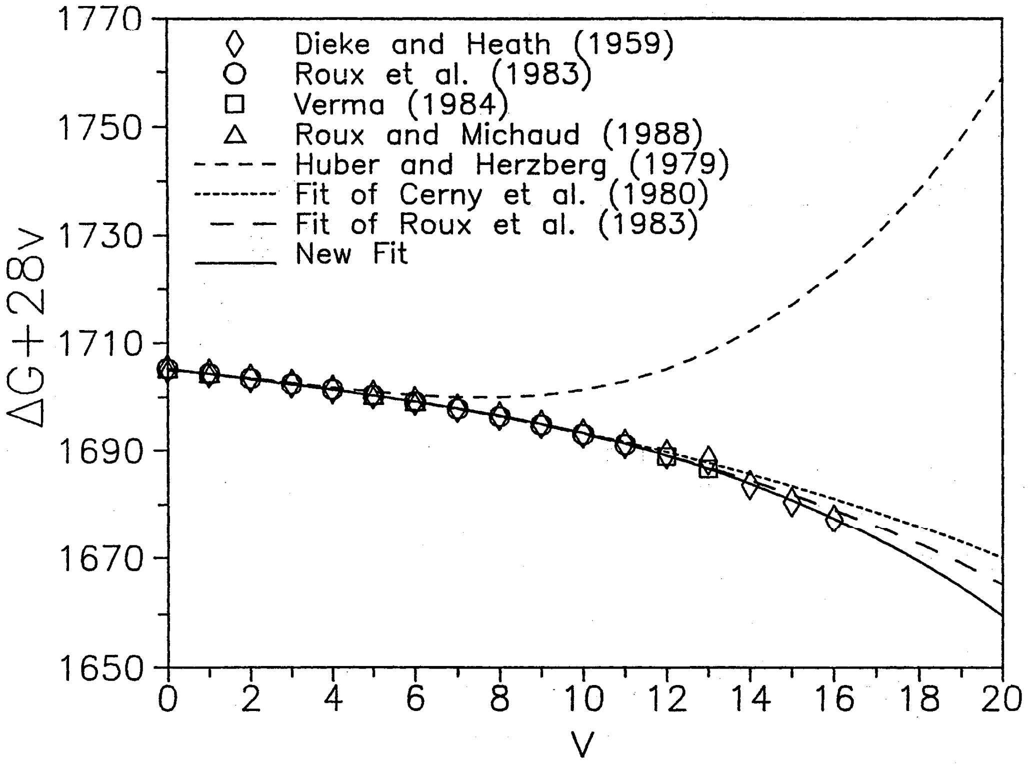

FIG. 5. Vibrational data and fits for the $B\ ^3\Pi_g$ state of N_2.

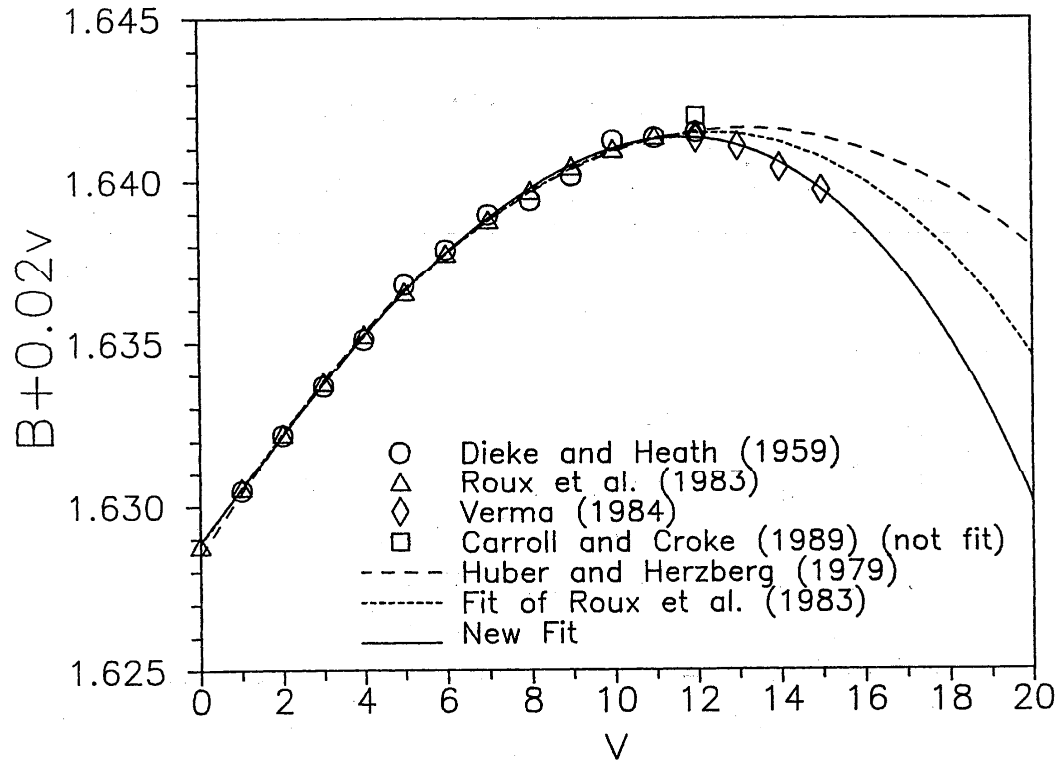

FIG. 6. Rotational data and fits for the $B\ ^3\Pi_g$ state of N_2.

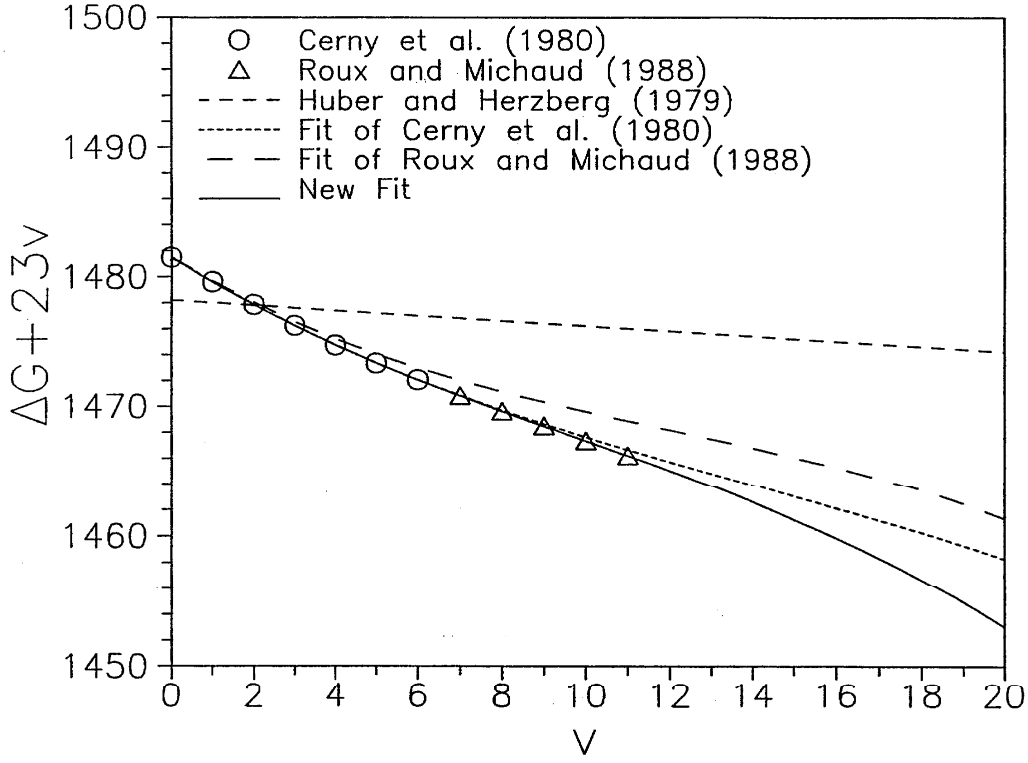

FIG. 7. Vibrational data and fits for the $W\ ^3\Delta_u$ state of N_2.

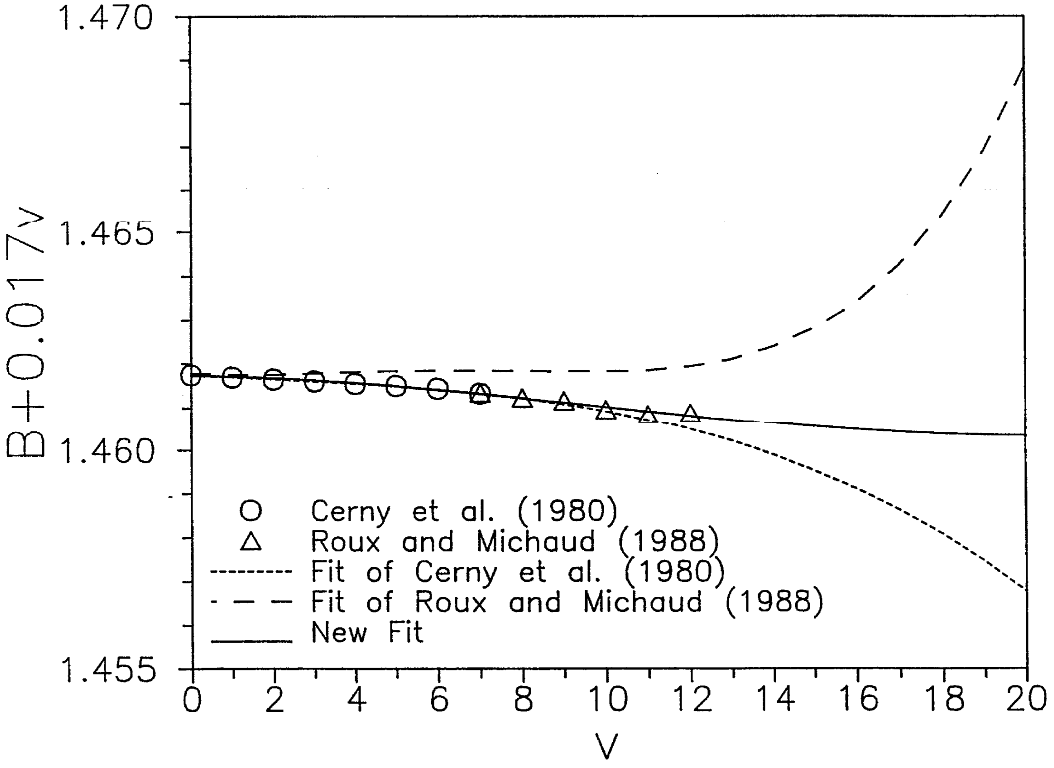

FIG. 8. Rotational data and fits for the $W\ ^3\Delta_u$ state of N_2.

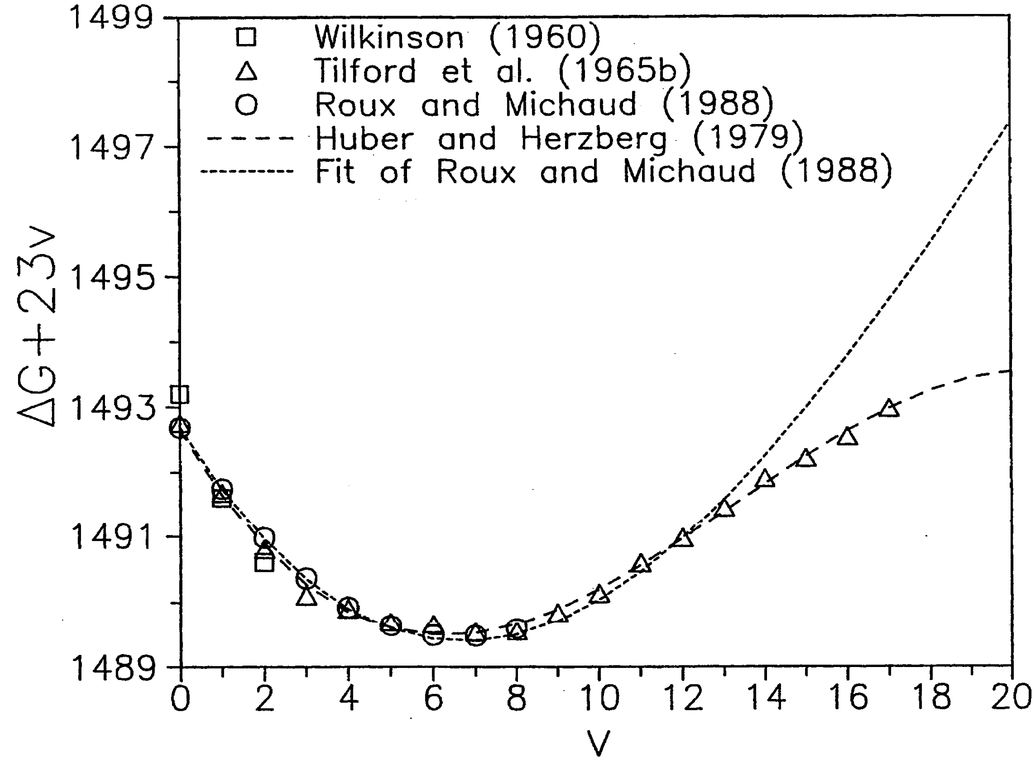

FIG. 9. Vibrational data and fits for the $B'\ ^3\Sigma_u^-$ state of N_2.

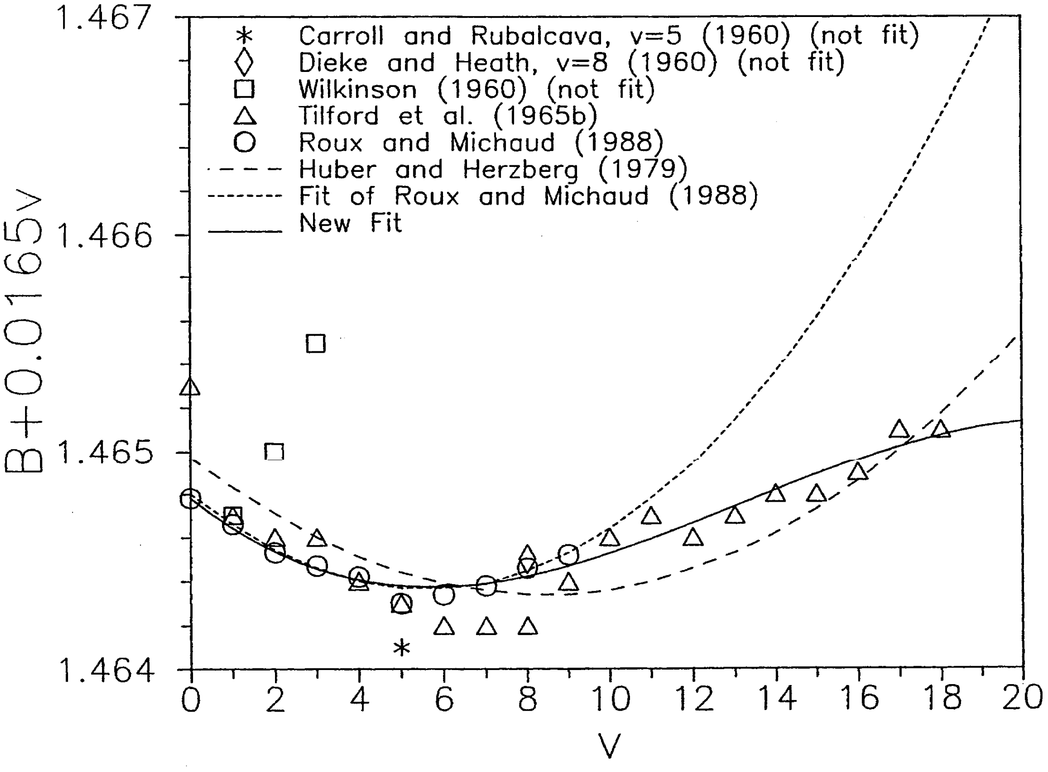

FIG. 10. Rotational data and fits for the $B'\ ^3\Sigma_u^-$ state of N_2.

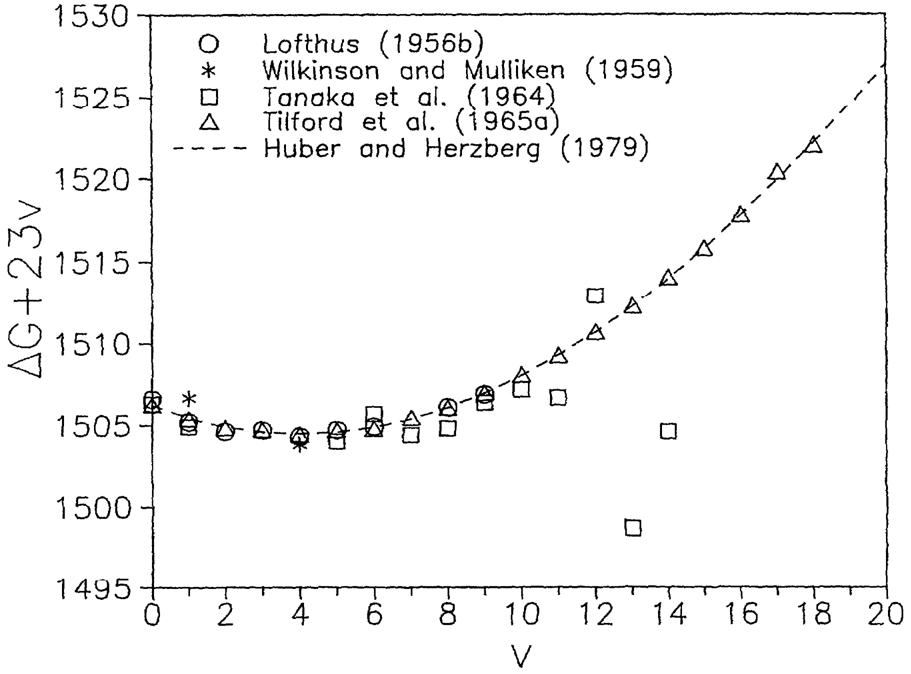

FIG. 11. Vibrational data and fit for the $a'\,^1\Sigma_u^-$ state of N_2.

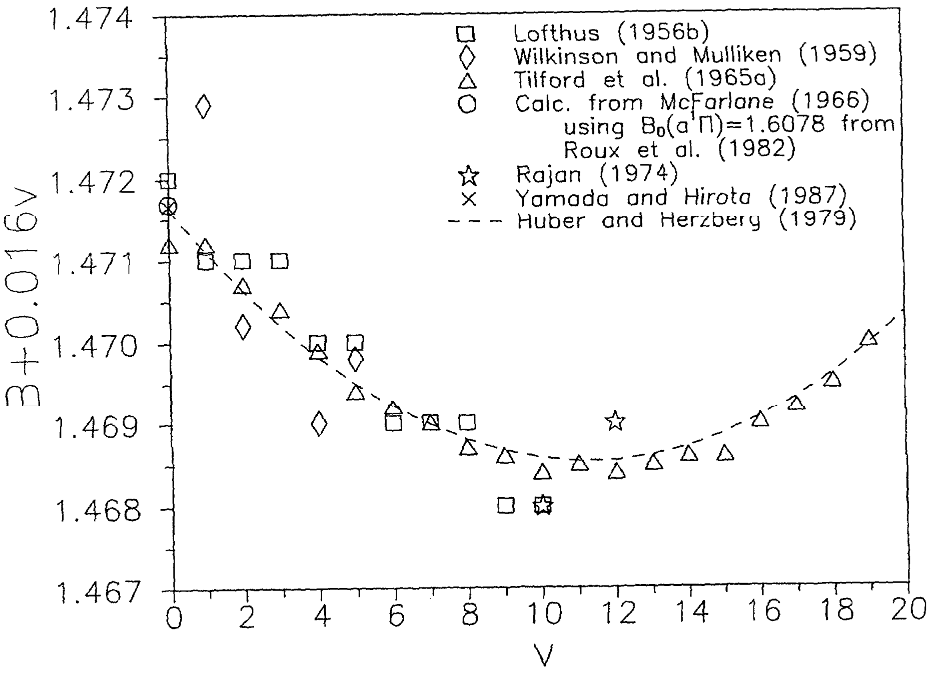

FIG. 12. Rotational data and fit for the $a'\,^1\Sigma_u^-$ state of N_2.

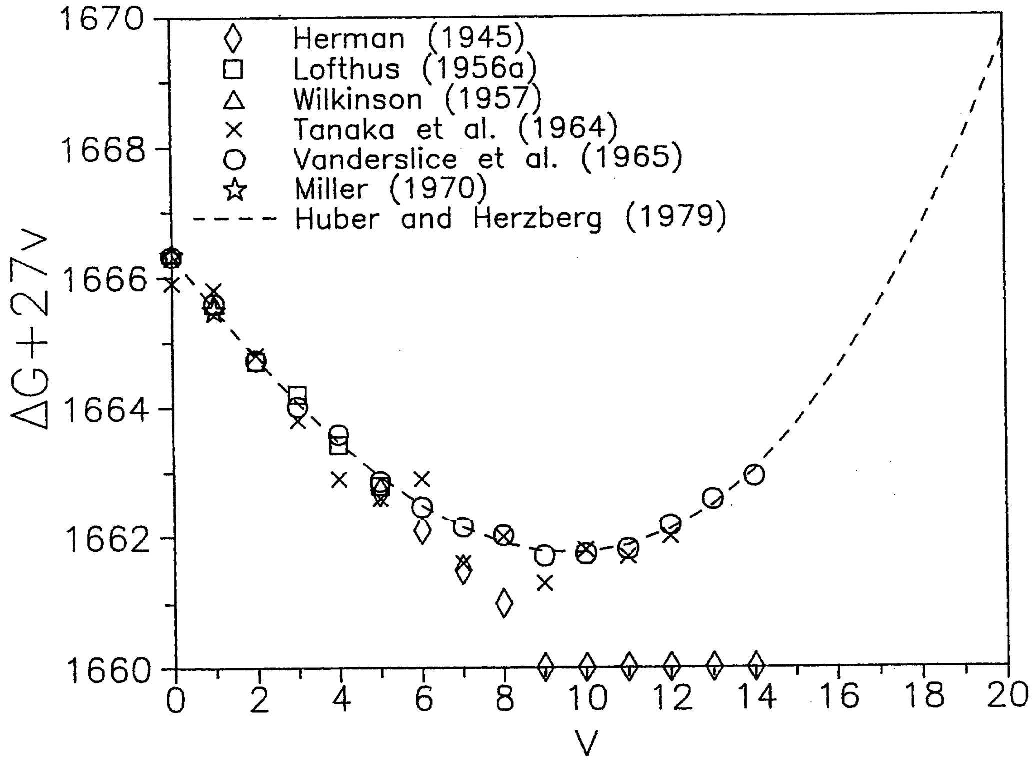

FIG. 13. Vibrational data and fit for the $a\ ^1\Pi_g$ state of N_2.

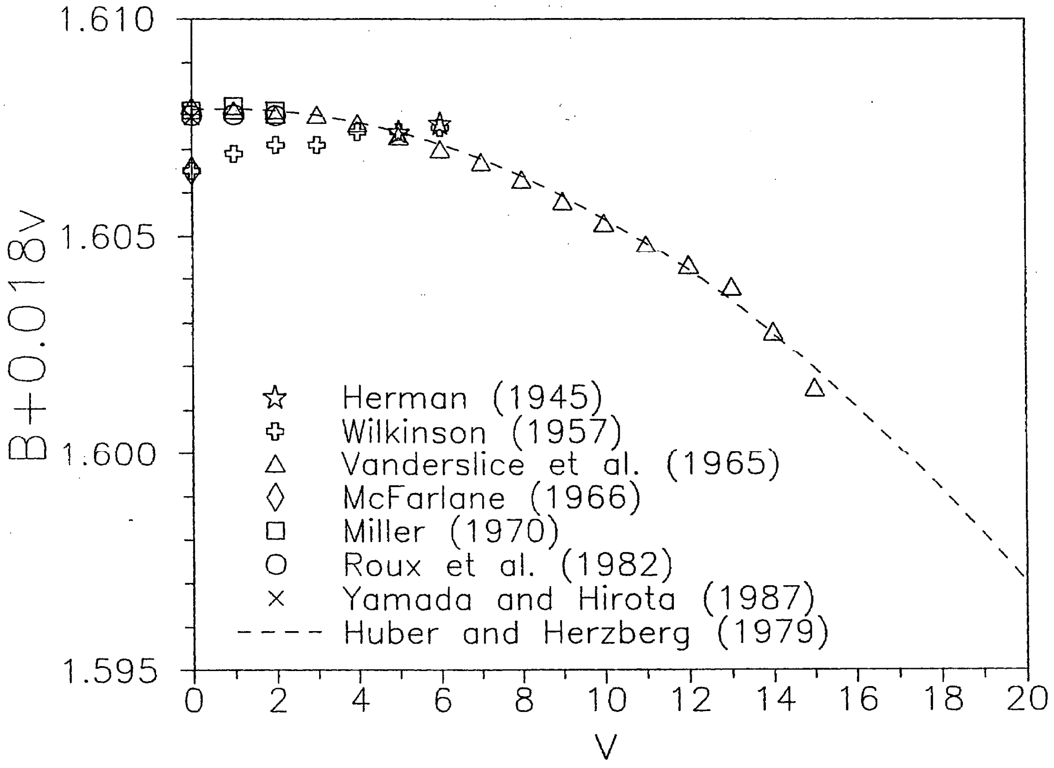

FIG. 14. Rotational data and fit for the $a\ ^1\Pi_g$ state of N_2.

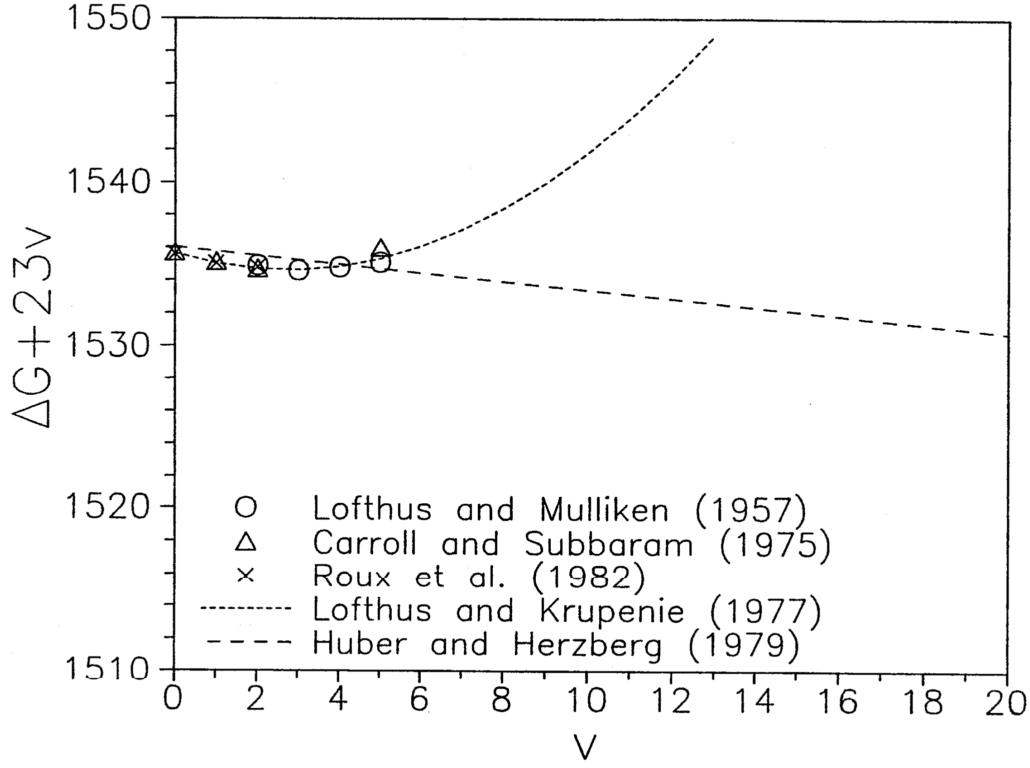

FIG. 15. Vibrational data and fits for the $w\ ^1\Delta_u$ state of N_2.

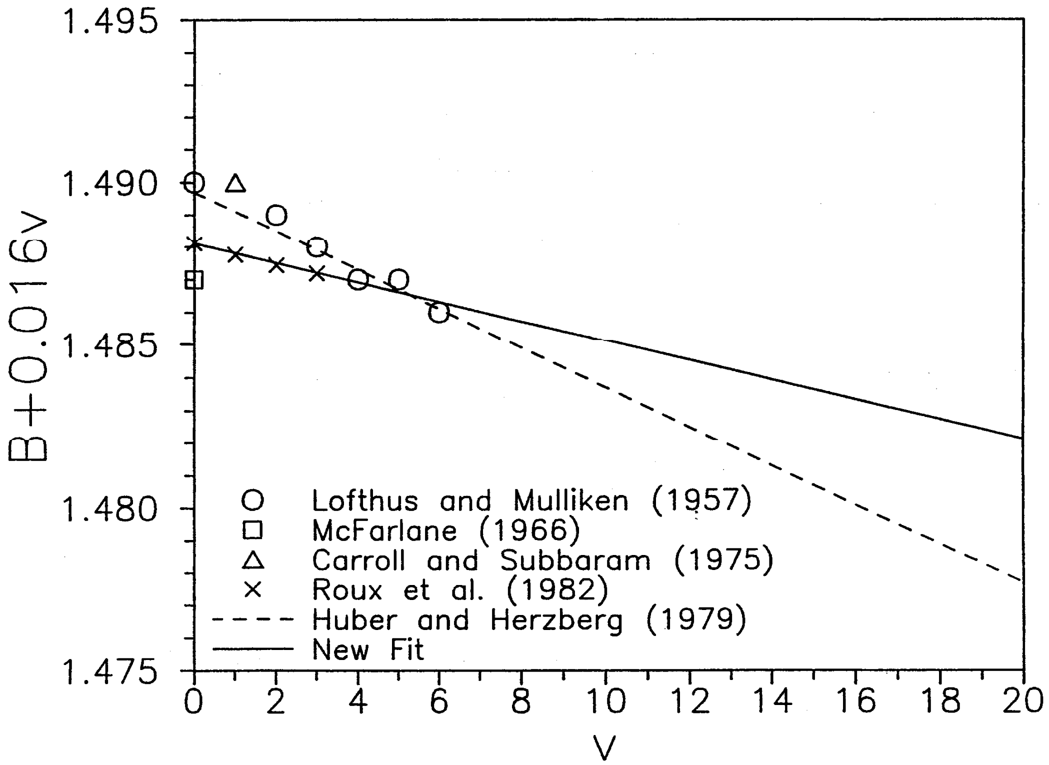

FIG. 16. Rotational data and fits for the $w\ ^1\Delta_u$ state of N_2.

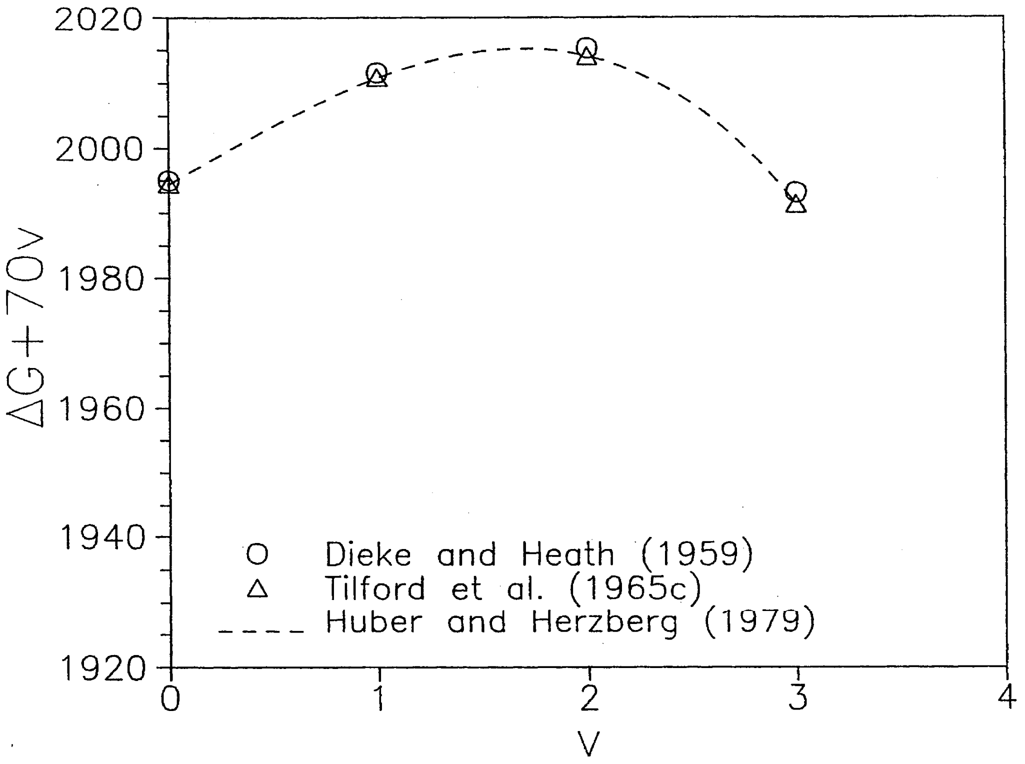

FIG. 17. Vibrational data and fit for the $C\ ^3\Pi_u$ state of N_2.

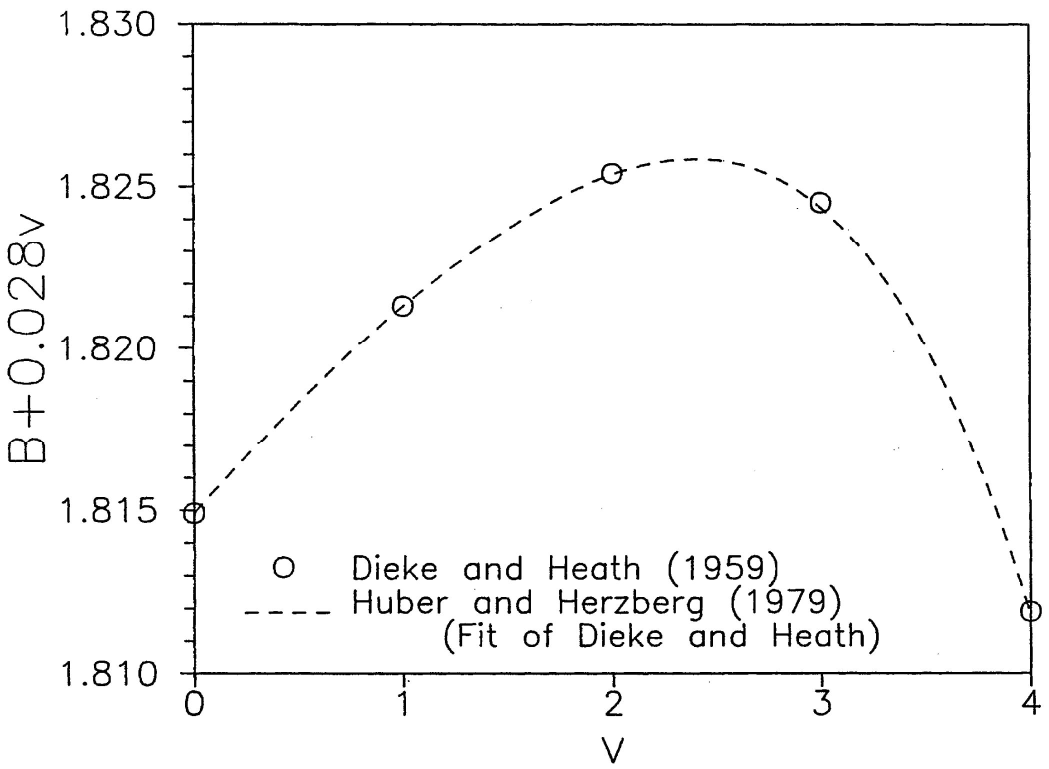

FIG. 18. Rotational data and fit for the $C\ ^3\Pi_u$ state of N_2.

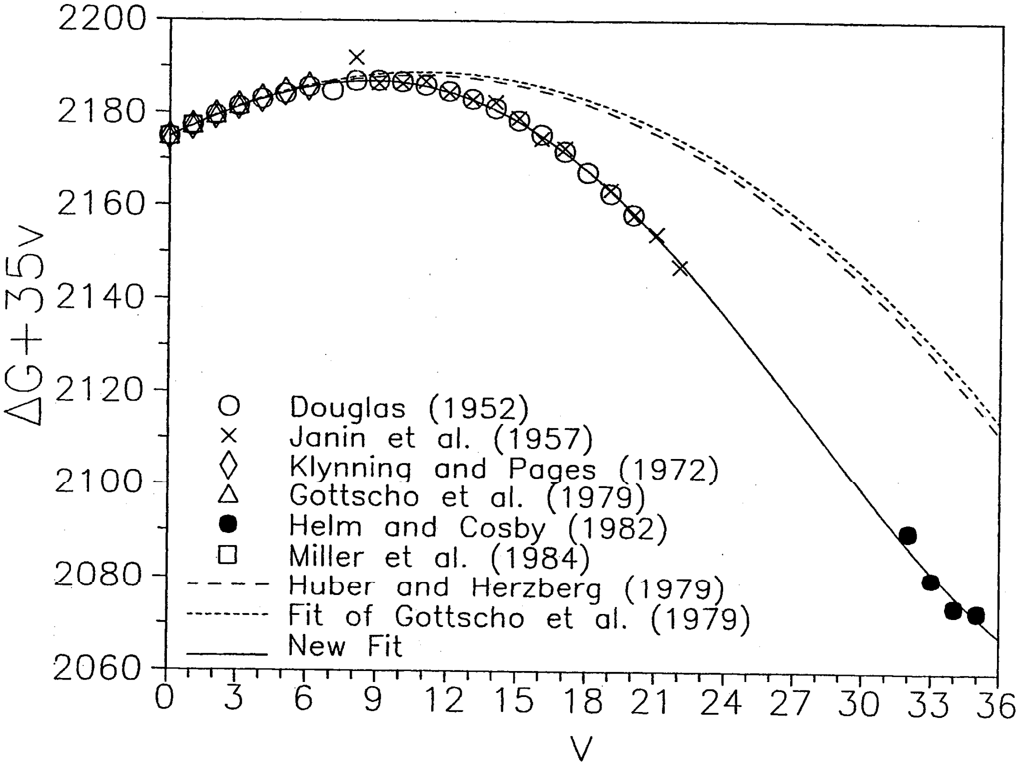

FIG. 19. Vibrational data and fits for the $X\ ^2\Sigma_g^+$ state of N_2^+.

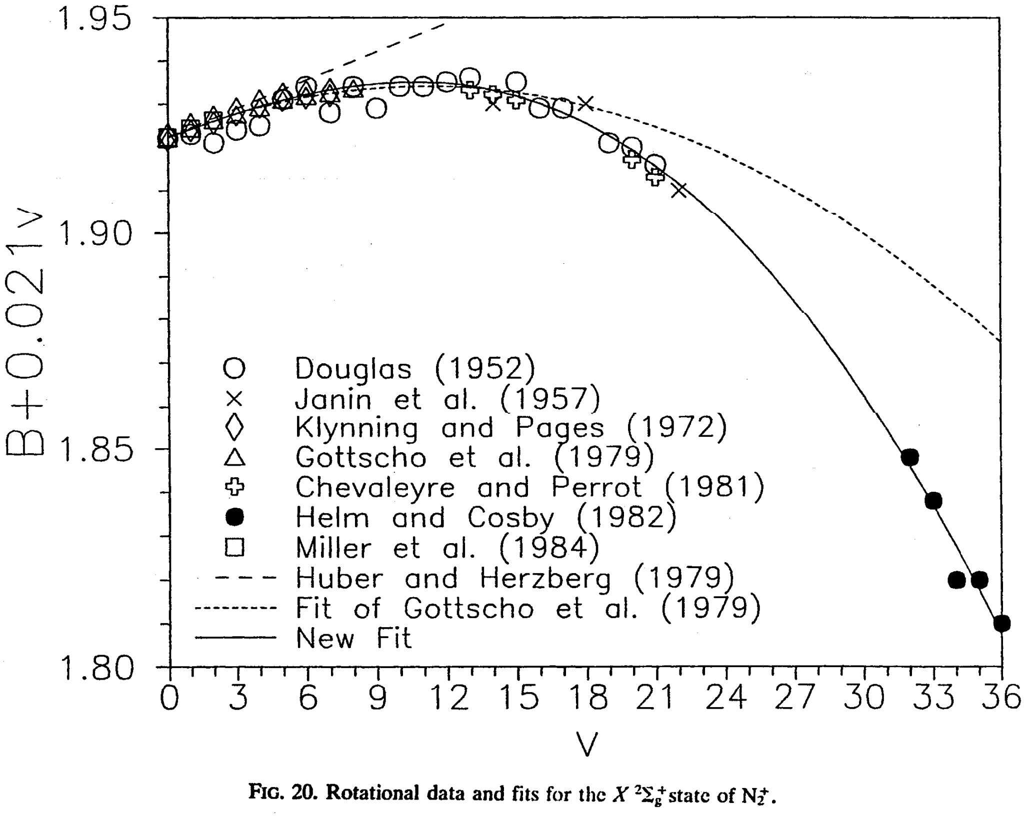

FIG. 20. Rotational data and fits for the $X\ ^2\Sigma_g^+$ state of N_2^+.

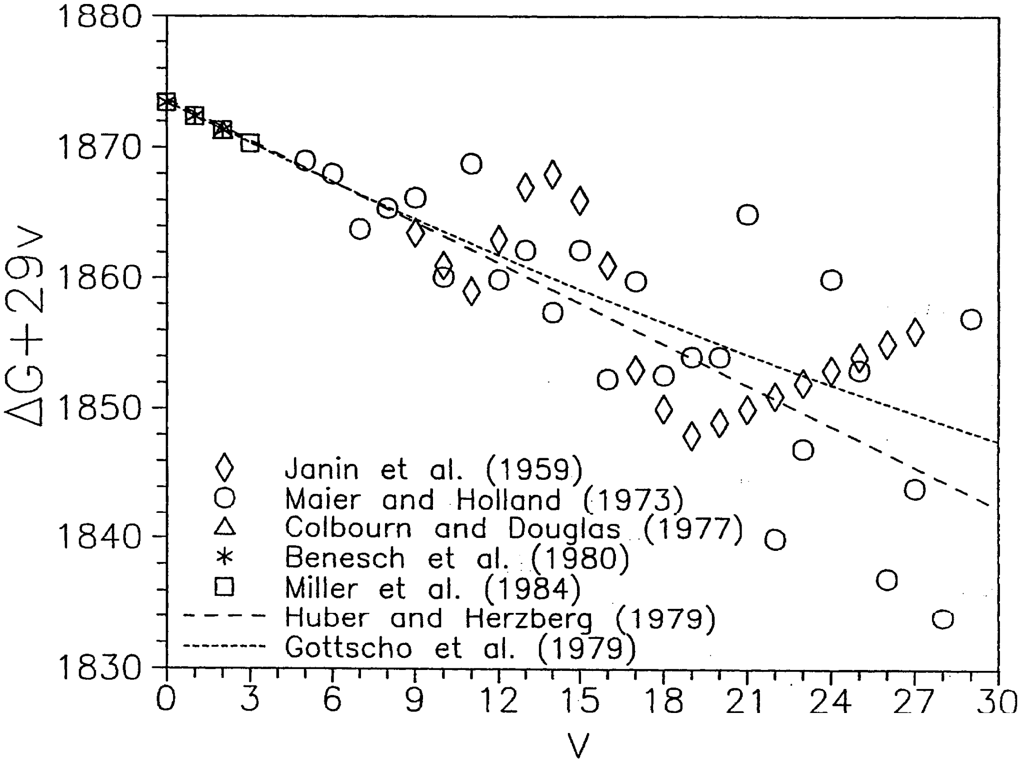

FIG. 21. Vibrational data and fits for the $A\ ^2\Pi_u$ state of N_2^+.

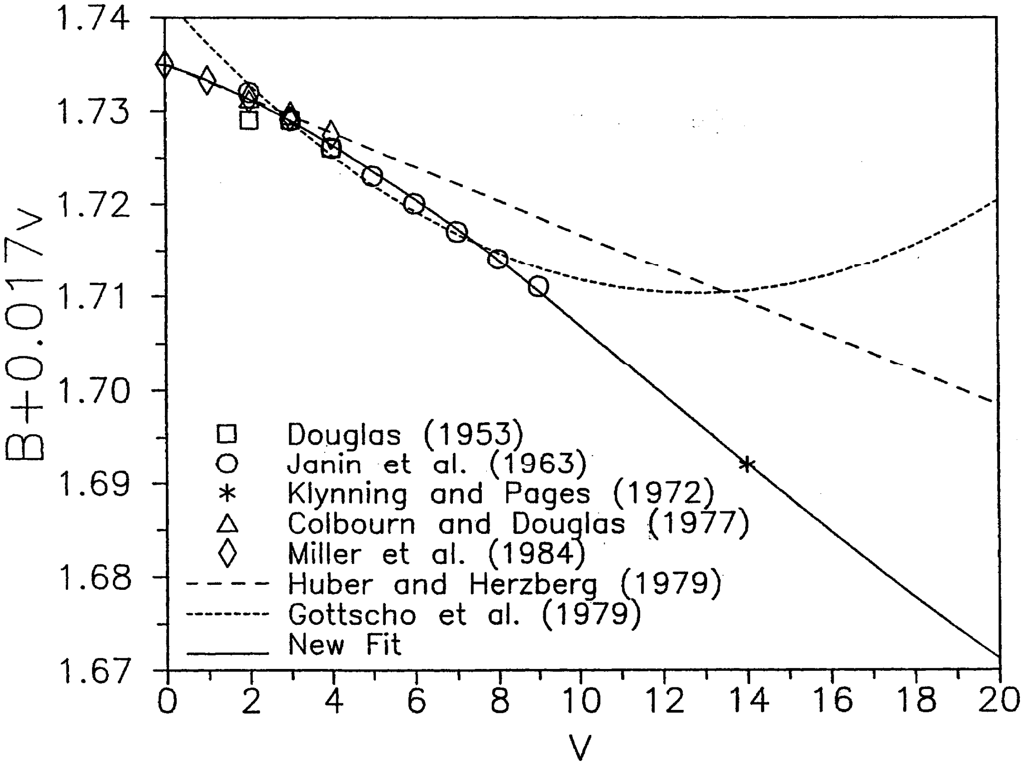

FIG. 22. Rotational data and fits for the $A\ ^2\Pi_u$ state of N_2^+.

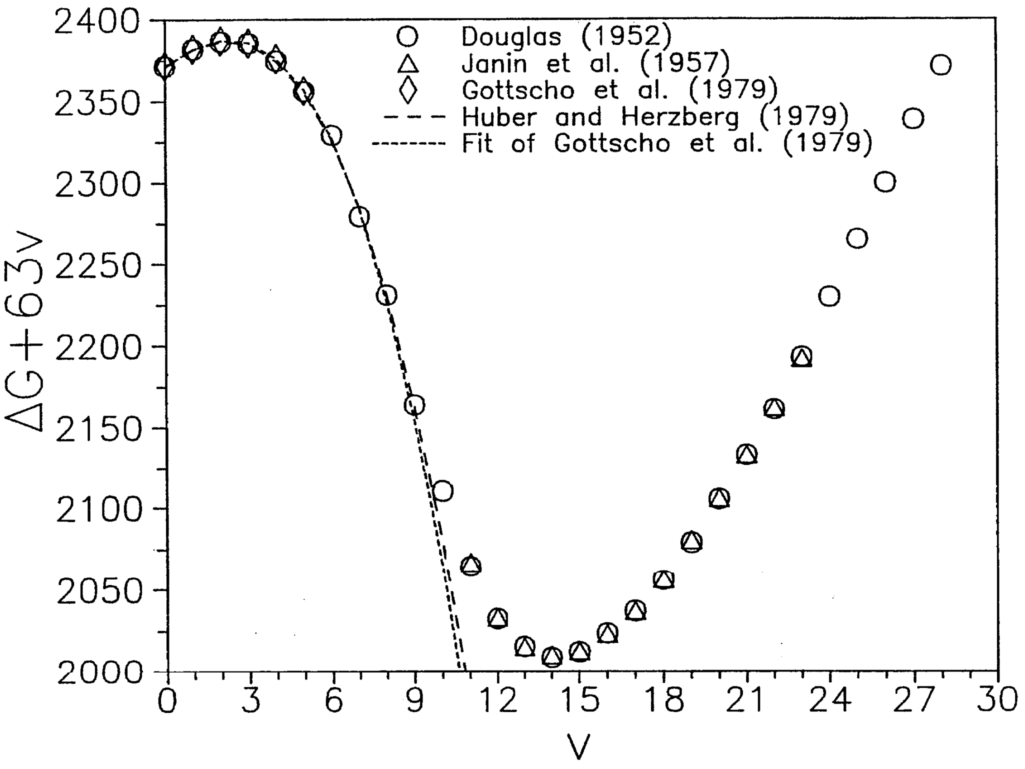

FIG. 23. Vibrational data and fits for the $B\ ^2\Sigma_u^+$ state of N_2^+.

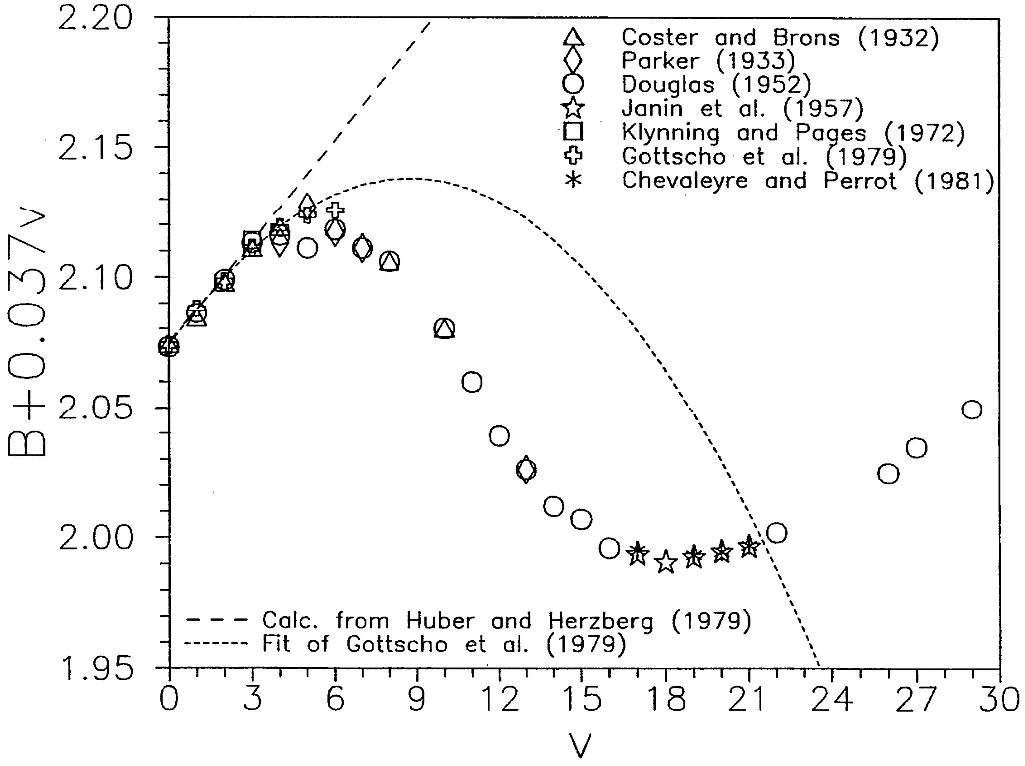

FIG. 24. Rotational data and fits for the $B\ ^2\Sigma_u^+$ state of N_2^+.

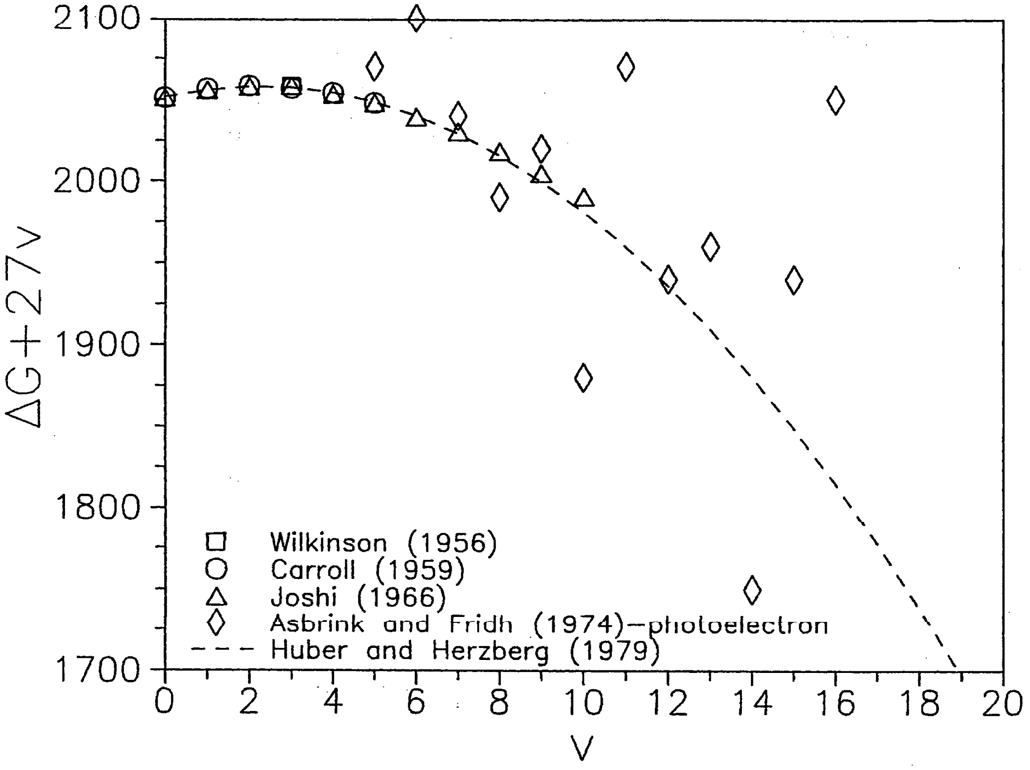

FIG. 25. Vibrational data and fit for the $C\ ^2\Sigma_u^+$ state of N_2^+.

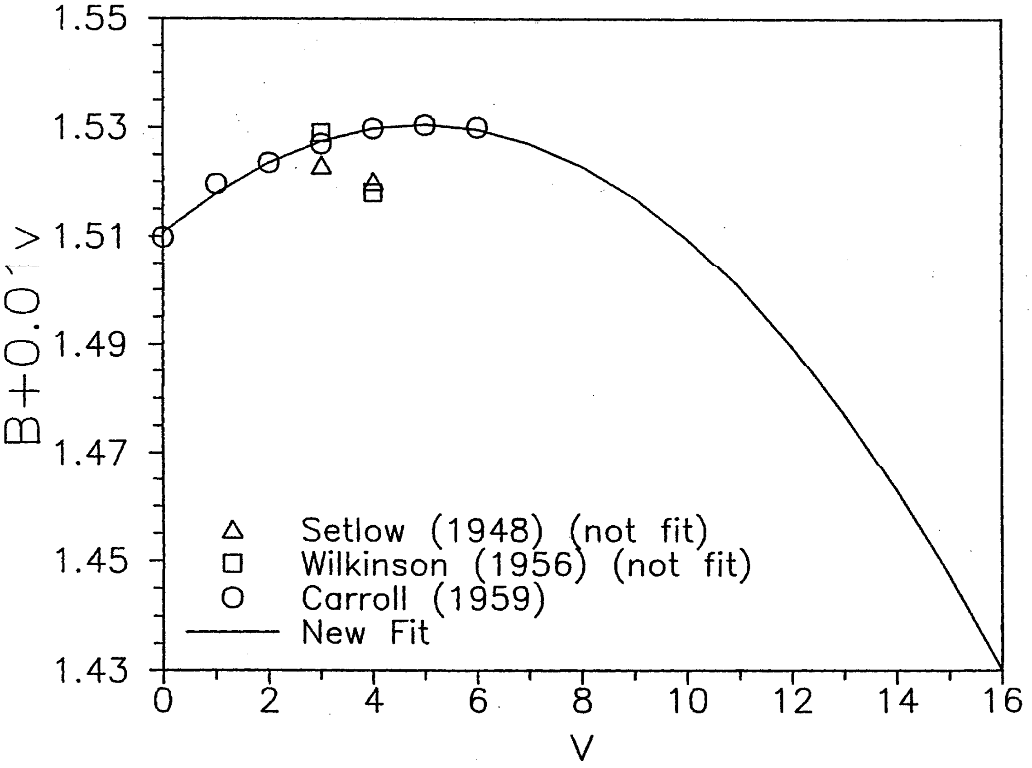

FIG. 26. Rotational data and fit for the $C\ ^2\Sigma_u^+$ state of N_2^+.

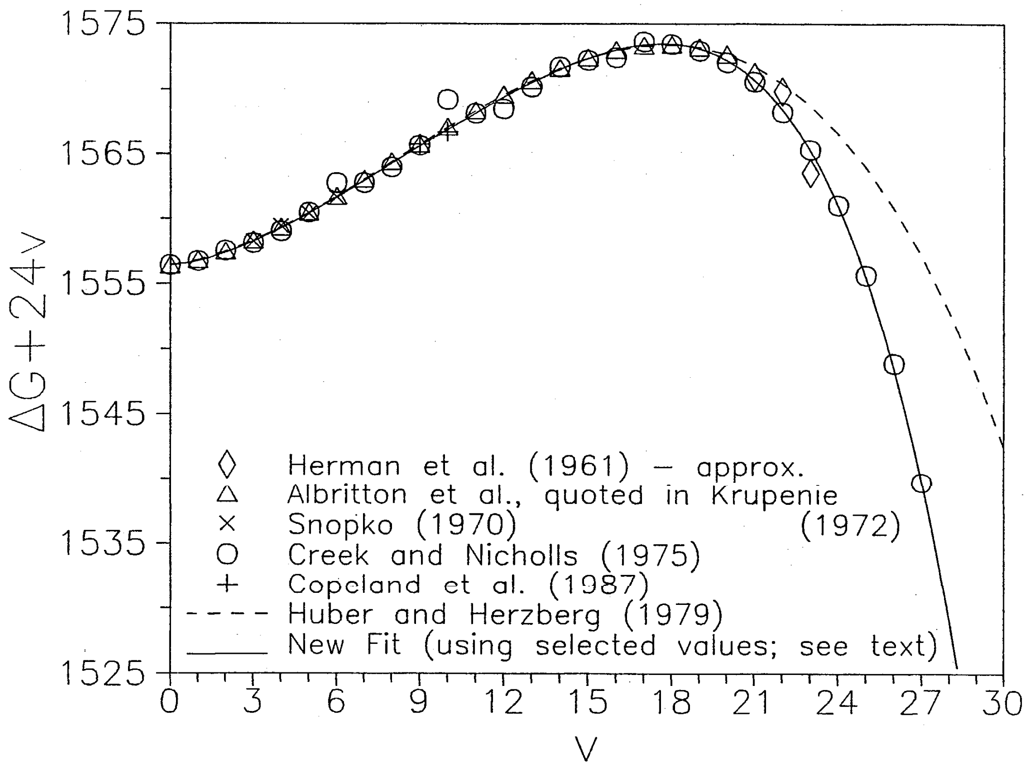

FIG. 27. Vibrational data and fits for the $X\ ^3\Sigma_g^-$ state of O_2.

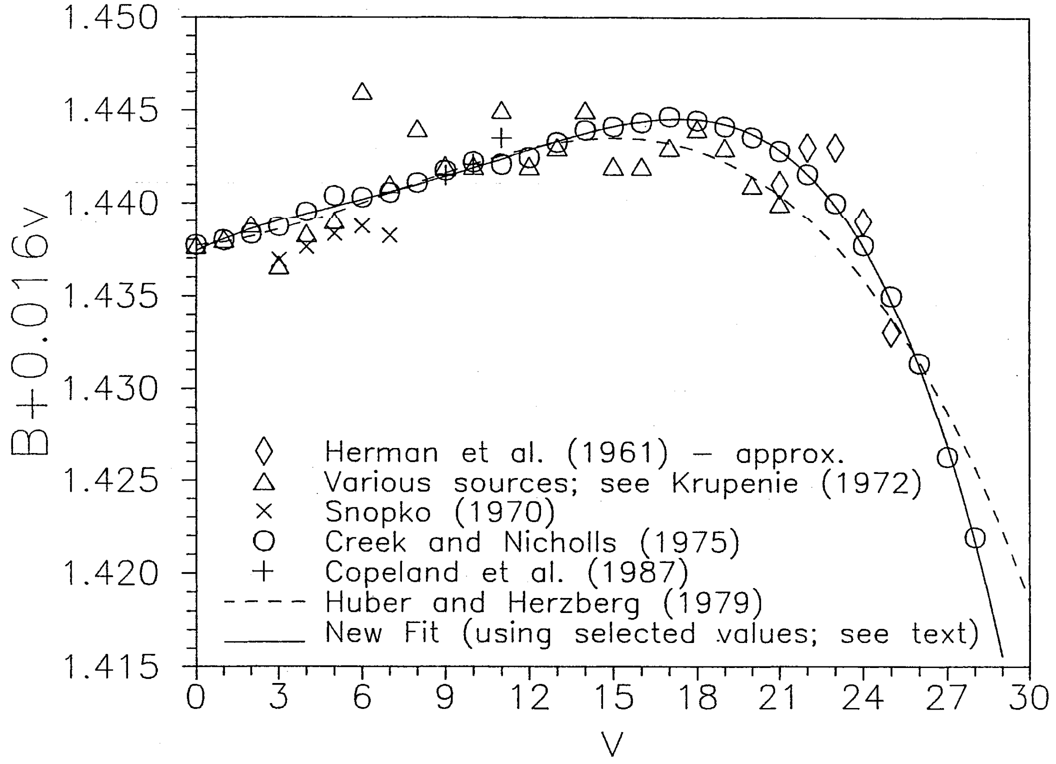

FIG. 28. Rotational data and fits for the $X\ ^3\Sigma_g^-$ state of O_2.

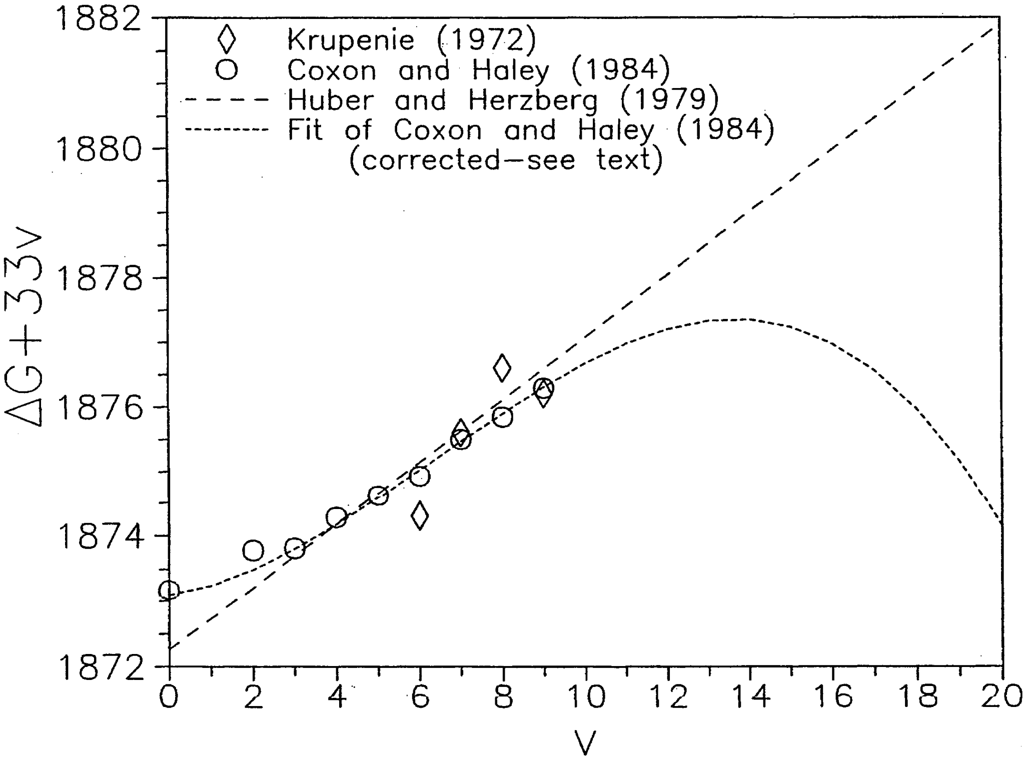

FIG. 29. Vibrational data and fits for the $X\ ^2\Pi_g$ state of O_2^+.

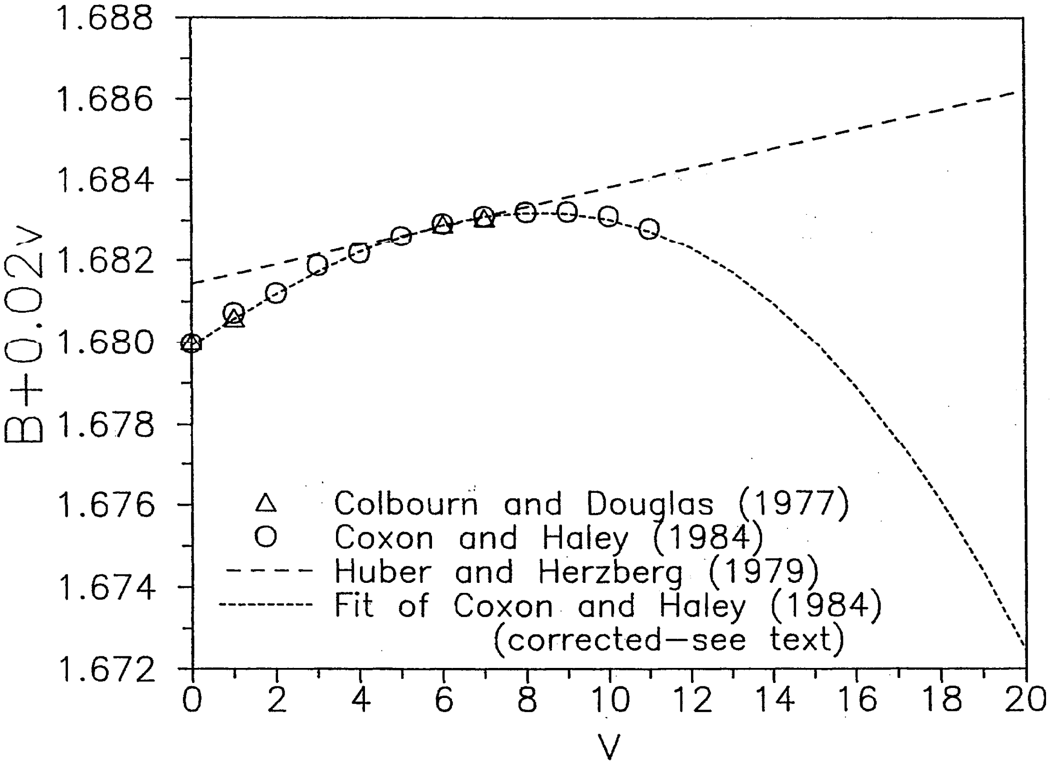

FIG. 30. Rotational data and fits for the $X\ ^2\Pi_g$ state of O_2^+.

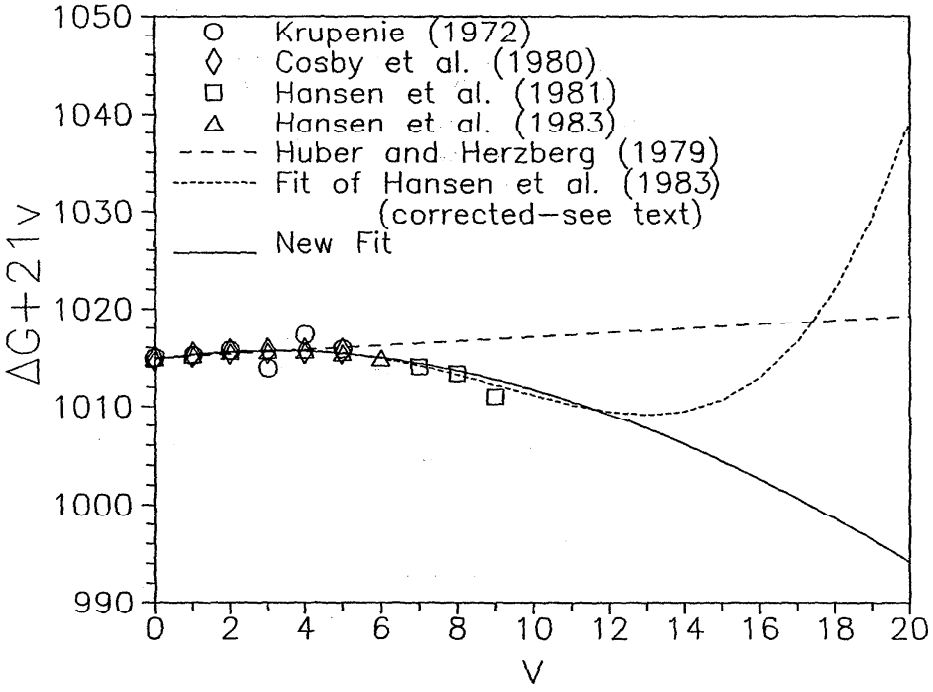

FIG. 31. Vibrational data and fits for the $a\ ^4\Pi_u$ state of O_2^+.

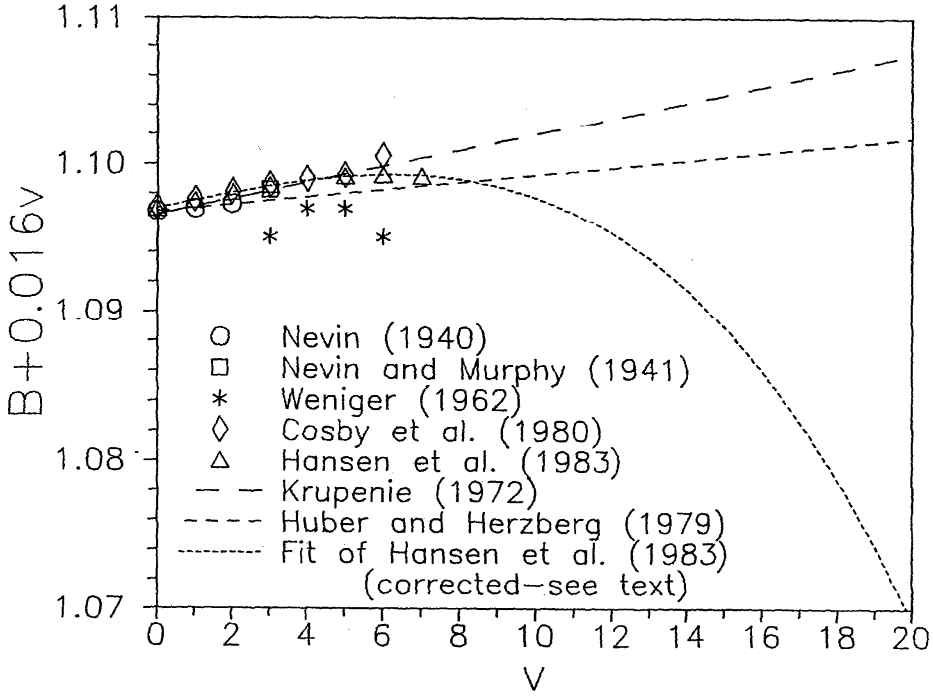

FIG. 32. Rotational data and fits for the $a\ ^4\Pi_u$ state of O_2^+.

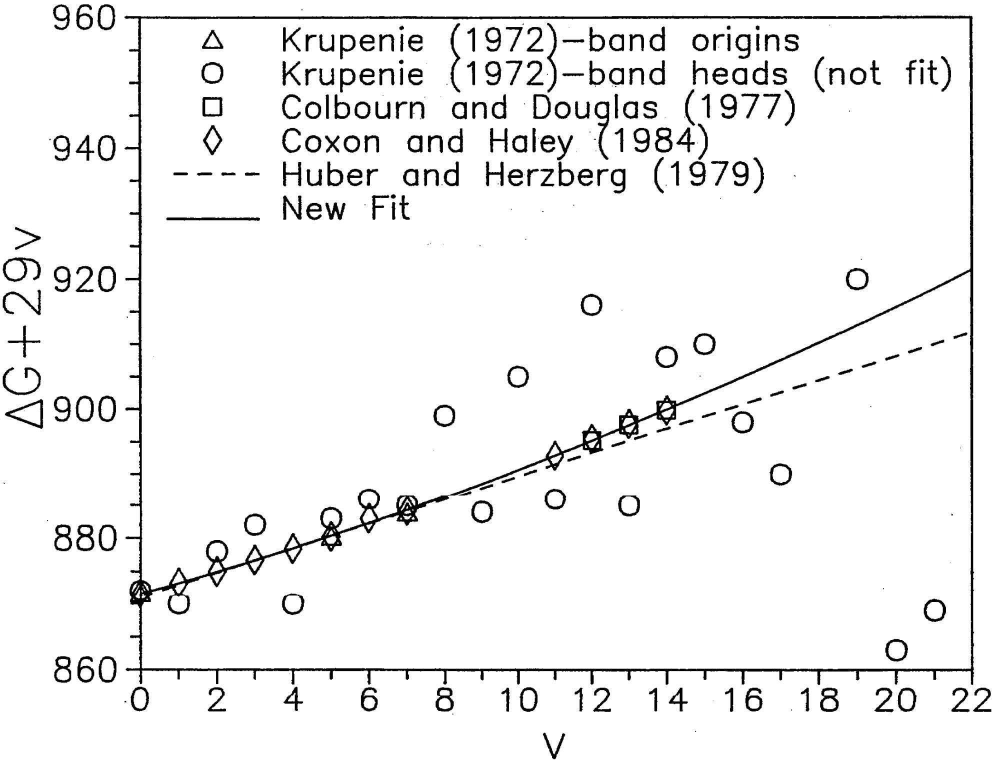

FIG. 33. Vibrational data and fits for the $A\ ^2\Pi_u$ state of O_2^+.

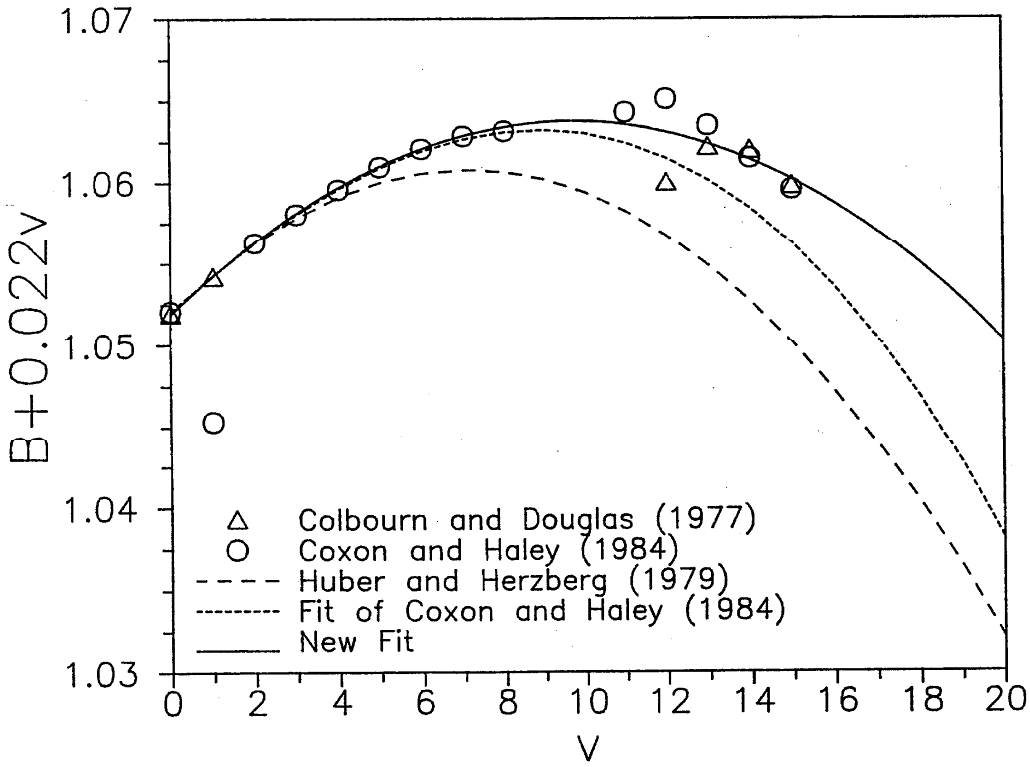

FIG. 34. Rotational data and fits for the $A\ ^2\Pi_u$ state of O_2^+.

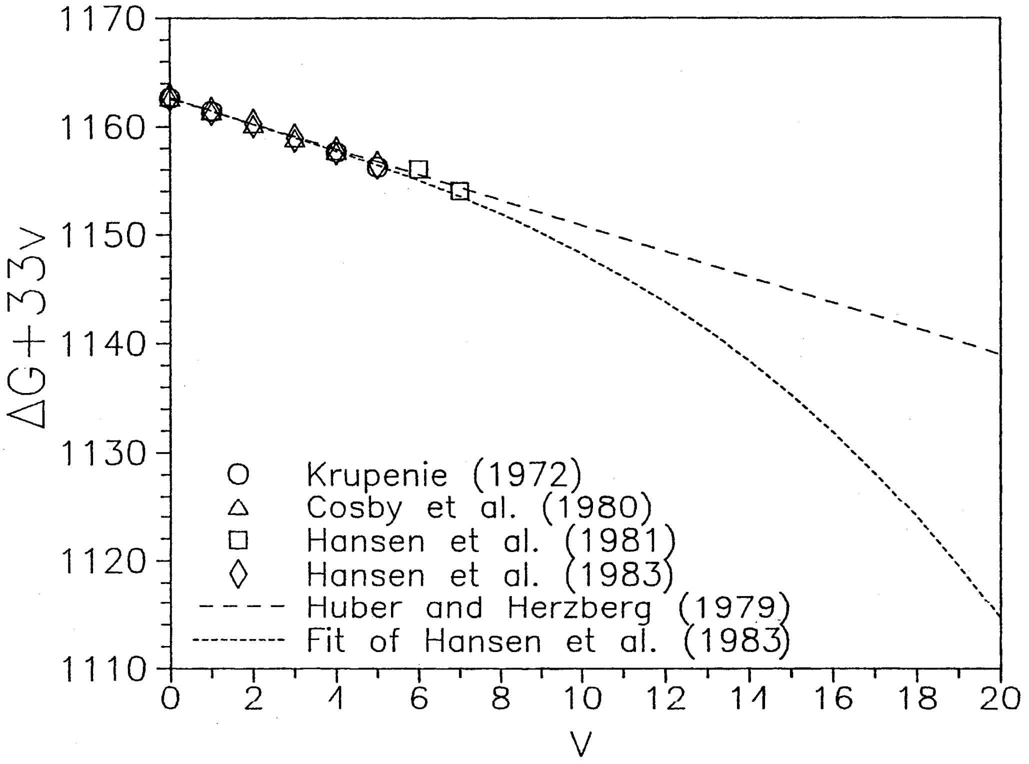

FIG. 35. Vibrational data and fits for the $b\ ^4\Sigma_g^-$ state of O_2^+.

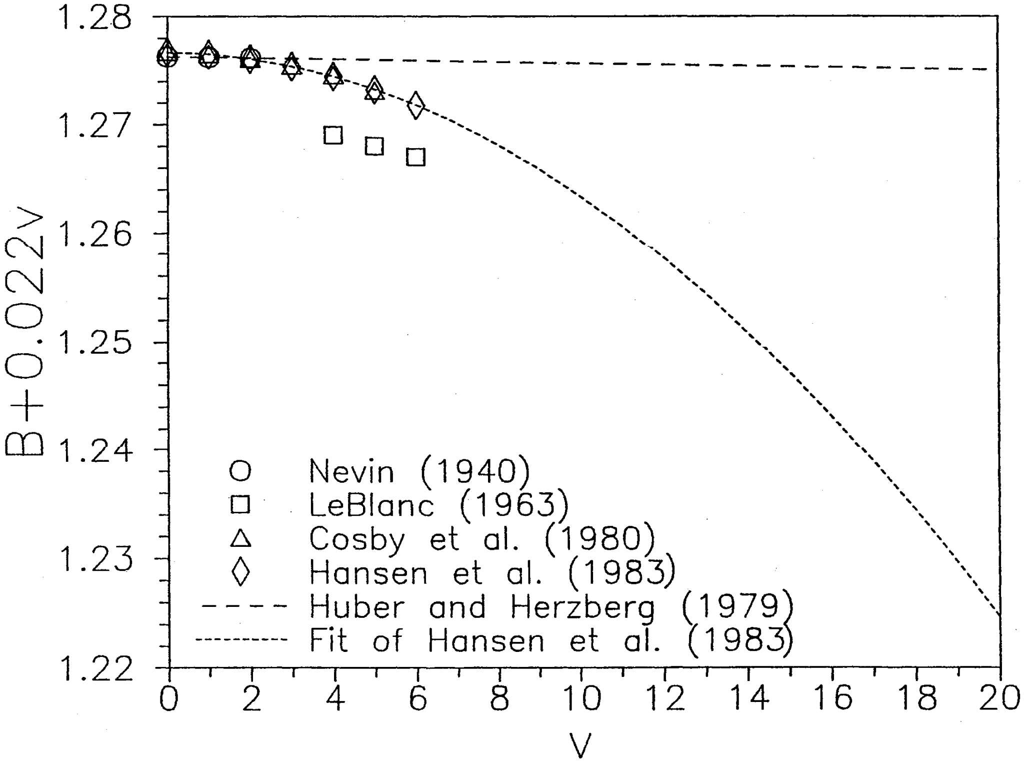

FIG. 36. Rotational data and fits for the $b\ ^4\Sigma_g^-$ state of O_2^+.

5. Acknowledgements

The authors thank C. C. Lin for an interesting discussion relevant to this work, P. C. Cosby, J. R. Fuhr, J.-Y. Roncin, and R. D. Verma for providing recent spectroscopic data, and a referee for helpful comments. This research was funded by the U.S. Defense Nuclear Agency under contract number DNA 001–88–C–0046.

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