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The Determination of Molecular Structure From Rotational Spectra

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The physical interpretation as well as the accuracy of structural parameters derived from spectroscopic effective moments of inertia is limited by vibration-rotation perturbations. It has recently been shown, however, that the effective moments may be converted to the moments of the average molecular configuration by corrections which involve only the harmonic vibrational force constants.[1,2] To a good approximation, the entire effect of anharmonicity is absorbed in displacing the average configuration from the equilibrium one, and this usually gives the dominant part of the zero-point vibrational contributions to moments of inertia.[2,3] Thus, often the isotopic dependence of the zero-point effects, which presents the chief difficulty in structure analysis, is primarily due to the isotopic variation of the average molecular configuration. In this paper, we shall consider the magnitude of these isotopic variations and their influence on structure determinations.

It is now well established that deuterium substitution has an appreciable effect on the average molecular structure.[3,4] For heavier atoms isotopic variations in average structural parameters are quite small, as illustrated in Table I. These slight isotopic changes in the actual parameters can give rise to much larger errors in calculated parameters, however, as the usual methods of structure analysis magnify the effect of isotopic variations. Fig. 1 illustrates this for a linear triatomic molecule. If replacing an end atom m_1 by a heavier isotope shrinks the R_{12} and R_{23} bonds by δ_1 and δ_3, then the moment of inertia is changed by

$$\Delta I = \mu z_1^2 + 2(m_1' z_1' \delta_1 - m_3 z_3' \delta_3), \qquad (1)$$

where z_i is the zero-point average distance of m_i from the center of mass, $\mu = M\Delta m_1/M'$, and the primes refer to the substituted species. Similar equations obtain for substitution of m_2 or m_3. As the factors $2m_1'z_1'$ and $2m_3z_3'$ which magnify δ_1 and δ_3 are negative, the apparent coordinate $\mathcal{Z}_1$ calculated from $\mu\mathcal{Z}_1^2 = \Delta I$ is always too small in magnitude. The apparent bond lengths $\mathcal{R}_{12} = \mathcal{Z}_2 - \mathcal{Z}_1$ and $\mathcal{R}_{23}$ may be either too small or too large, however. In Fig. 1 the errors in the apparent coordinates were evaluated for $\Delta m_i = 1$ substitutions in $O^{16}C^{12}S^{32}$ by assuming $\delta = 10^{-4}$ A for the bond or bonds adjacent to the substituted atom. The masses of m_1 and m_2 were varied, with other parameters fixed, in order to examine the role of distance from the center of mass. The error in $\mathcal{Z}_2$, which is relatively large even for $z_2 > 0.5$ A, is catastrophic when z_2 is small, and $\mathcal{Z}_2$ becomes imaginary within the shaded regions.

Similar consideratdons explain the large variations in the "r_o" bond lengths of OCS shown in Table II. Thus, the results derived from the first two pairs of isotopes can be accounted for with δ's similar to those of Table I for the CO^{18} and CS^{34} bonds, whereas the close agreement of the results for the third and fourth pairs is expected if the δ's for C^{13} and S^{34} substitution are roughly additive.

It is also found that "r_s" structures,[5] while displaying much better isotopic consistency than r_o structures, can deviate seriously from the actual structure. For more complicated molecules, relations analogous to (1) indicate that several examples of apparent structural peculiarities can be attributed to the neglect of the isotopic variations.

References

1. T. Oka. J. Phys. Soc. Japan 15, 2274 (1960); Y. Morino, K. Kuchitsu, and T. Oka. J. Chem. Phys. 36, 1108 (1962).

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Table I. Variation of effective and average bond lengths of CO and CS molecules.

Molecule	r_e	r_o	$\langle r \rangle$	Ref.
$C^{12}O^{16}$	1.1282	1.13088	1.13228	a
$C^{13}O^{16}$		1.13082	1.13219	
$C^{12}O^{18}$		1.13081	1.13219	
$C^{13}O^{18}$		1.13075	1.13209	
$C^{12}S^{32}$	1.5349	1.53771	1.53917	b
$C^{12}S^{34}$		1.53768	1.53913	
$C^{13}S^{32}$		1.53762	1.53905	

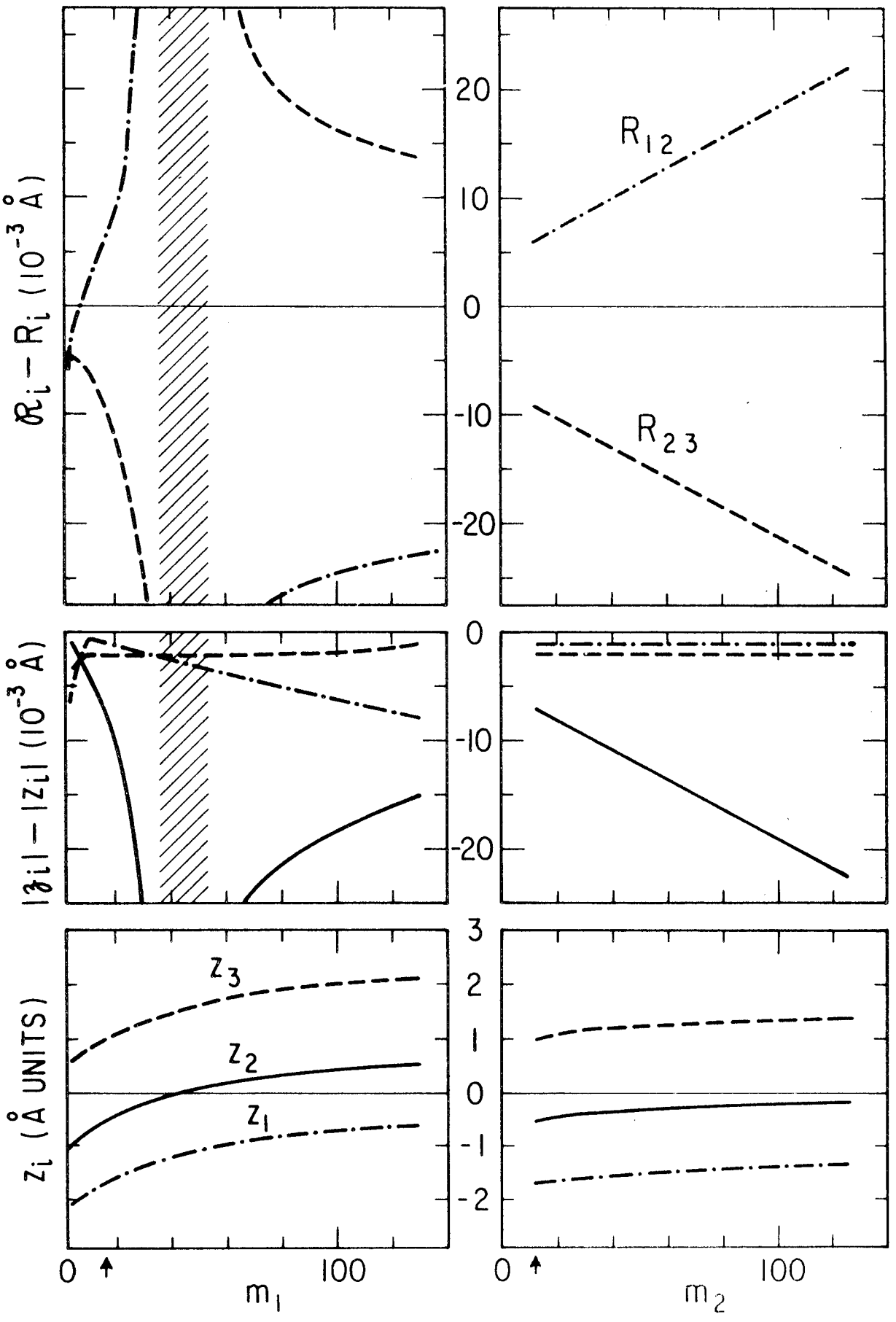
[a] B. Rosenblum, A. H. Nethercot, and C. H. Townes, Phys. Rev. 109, 400 (1958).

[b] R. C. Mockler and G. R. Bird, Phys. Rev. 98, 1837 (1955).

Table II. Variation of effective bond lengths of OCS.

Isotopic pairs[a]	r_o(CO)	r_o(CS)
$O^{16}C^{12}S^{32}, O^{18}C^{12}S^{32}$	1.1552	1.5653
$O^{16}C^{12}S^{32}, O^{16}C^{12}S^{34}$	1.1647	1.5576
$O^{16}C^{12}S^{32}, O^{16}C^{13}S^{32}$	1.1629	1.5591
$O^{16}C^{12}S^{34}, O^{16}C^{13}S^{34}$	1.1625	1.5594

[a] From C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Co., Inc., N.Y., 1955), p. 42.


$\mathcal{R}_i - R_i$ (10^{-3} Å)
20
10
0
-10
-20
R_{12}
R_{23}
$|\mathcal{Z}_i| - |z_i|$ (10^{-3} Å)
0
-10
-20
z_i (Å UNITS)
3
2
1
0
-1
-2
z_3
z_2
z_1
0
100
m_1
0
100
m_2

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