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THE DETERMINATION OF MOLECULAR STRUCTURE  
FROM ROTATIONAL SPECTRA

Victor W. Laurie and Dudley R. Herschbach

July 1962

## The Determination of Molecular Structure From Rotational Spectra

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July 1962

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.<sup>1,2</sup> 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.<sup>2,3</sup> 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.<sup>3,4</sup> 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  $\delta_1$  and  $\delta_3$ , then the moment of inertia is changed by

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

where  $z_1$  is the zero-point average distance of  $m_1$  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  $2m_3 z_3'$  which magnify  $\delta_1$  and  $\delta_3$  are negative, the apparent coordinate  $\rho_1$  calculated from  $\mu \rho_1^2 = \Delta I$  is always too small in magnitude. The apparent bond lengths  $R_{12} = \rho_2 - \rho_1$  and  $R_{23}$  may be either too small or too large, however. In Fig. 1 the errors in the apparent coordinates were evaluated for  $\Delta m_1 = 1$  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  $\rho_2$ , which is relatively large even for  $z_2 > 0.5$  A, is catastrophic when  $z_2$  is small, and  $\rho_2$  becomes imaginary within the shaded regions.

Similar considerations explain the large variations in the " $r_0$ " bond lengths of OCS shown in Table II. Thus, the results derived from the first two pairs of isotopes can be accounted for with  $\delta$ '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  $\delta$ 's for  $C^{13}$  and  $S^{34}$  substitution are roughly additive.

It is also found that " $r_s$ " structures,<sup>5</sup> while displaying much better isotopic consistency than  $r_0$  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.

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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.
$^{12}_O^{16}C$	1.1282	1.13088	1.13228	a
$^{13}_O^{16}C$		1.13082	1.13219	
$^{12}_O^{18}C$		1.13081	1.13219	
$^{13}_O^{18}C$		1.13075	1.13209	
$^{12}_S^{32}C$	1.5349	1.53771	1.53917	b
$^{12}_S^{34}C$		1.53768	1.53913	
$^{13}_S^{32}C$		1.53762	1.53905	

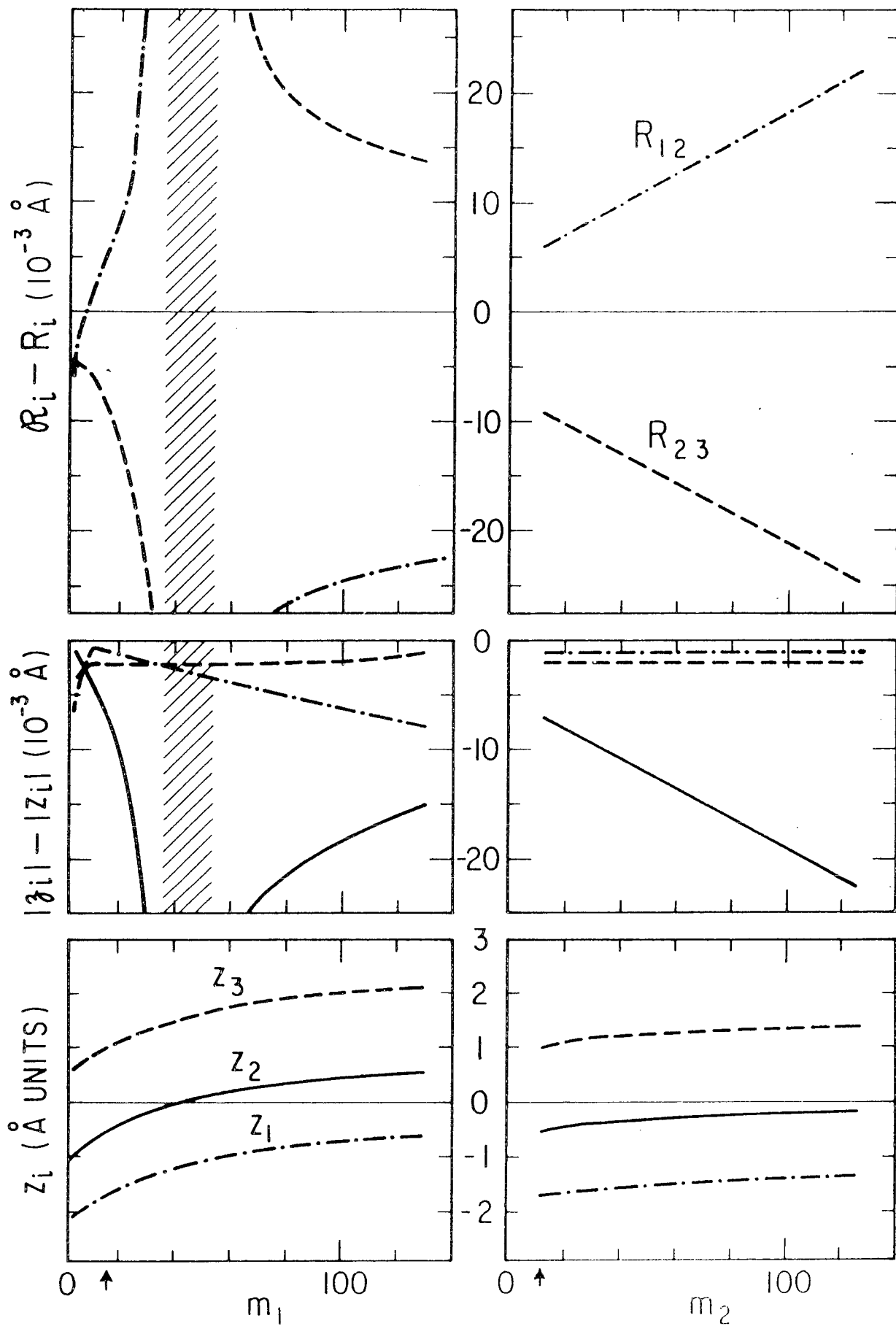
<sup>a</sup>B. Rosenblum, A. H. Nethercot, and C. H. Townes, Phys. Rev. 109, 400 (1958).

<sup>b</sup>R. C. Mockler and G. R. Bird, Phys. Rev. 98, 1837 (1955).

Table II. Variation of effective bond lengths of OCS.

Isotopic pairs <sup>a</sup>	$r_o$ (CO)	$r_o$ (CS)
$^{16}_O^{12}_C^{32}_S, ^{18}_O^{12}_C^{32}_S$	1.1552	1.5653
$^{16}_O^{12}_C^{32}_S, ^{16}_O^{12}_C^{34}_S$	1.1647	1.5576
$^{16}_O^{12}_C^{32}_S, ^{16}_O^{13}_C^{32}_S$	1.1629	1.5591
$^{16}_O^{12}_C^{34}_S, ^{16}_O^{13}_C^{34}_S$	1.1625	1.5594

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



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