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NOTES

A Radial Function for the Nuclear Quadrupolar Interaction of HCl

Kaiser has published (*1*) some comments on my paper (*2*). These comments are here discussed with further explanation of the previous calculations.

First of all, the derivation of a dependence on internuclear distance of some spectral property of a diatomic molecule, such as the effects in molecular spectra due to a gradient of the electric field at a nonspherical nucleus, is implicitly an assumption of the Born–Oppenheimer separation of electronic and nuclear motions. In recognition thereof, one logically proceeds to fit all available spectral data of a certain type, including all the various isotopic species, for a diatomic molecule in a given electronic state. If the fit yields reasonable values of the overdetermined parameters that satisfactorily reproduce all the input data according to standard statistical criteria, the results are rationally taken to be consistent with the underlying assumption; further effects are superfluous.

In the case of the nuclear quadrupolar data (*3*), in his analysis Kaiser used only the data for HCl, thus fitting only four experimental data to derive the values of three parameters, while omitting his data for DCl. Although his derived parameters adequately reproduce the experimental results of HCl, the average deviation of the values predicted therefrom for DCl corresponds to hundreds of standard errors of their measurement. However, an adequate method to use all the available isotopic data had been developed much earlier by Schlier (*4*). The method that I have used (*2*) is essentially a systematic development of Schlier's approach; by this means I have fitted (simultaneously, not serially as in the case of data for CN of another type discussed (*2*) in the same paper) all eight data points measured by Kaiser (*3*) to only five parameters (*2*), having reasonable values, that reproduce all the experimental data to within essentially one standard error of the values given by Kaiser (*3*). Thus there is no arbitrary choice of values of parameters. The inclusion in the fitting process of all the experimental data, appropriately weighted by the reciprocal squares of Kaiser's specified standard errors (*3*), is merely proper and inherently consistent with the derivation of a radial function. Moreover, the fact that all eight observed values are satisfactorily fitted by means of five parameters implies that these parameters have at least as much physical meaning as the three parameters deduced by Kaiser from four observed values.

On the basis of this satisfactory fit, my conclusion that "the invocation of the breakdown of the Born–Oppenheimer approximation is superfluous" is reasonable. Of course one recognizes that the Born–Oppenheimer treatment is an approximation, and that at some level of accuracy the deviations resulting from that approximation become significant with respect to the precision of experimental measurements. One has moreover a semiquantitative expectation of the upper limit of the relative magnitude of such deviations, although it may happen that fortuitous partial cancellation of contributing effects may lead to the approximation's having an effective range of validity apparently beyond the supposed limit. The ultimate test of the existence of such deviations is provided by additional and precise experimental data. Since Kaiser's report (*3*) of the few but precise data for the nuclear quadrupolar interaction in $H^{35}Cl$ and $D^{35}Cl$, further data for this molecular system are lacking; thus a definitive test is at present precluded. When more data become available, and if tests prove the fallibility of the approximation, then appropriate methods (*5*) to generate the radial dependence of any underlying physical effect may be applied. One should not simply postulate the "breakdown of the Born–Oppenheimer approximation" as a qualitative rationalization of any effects unexplained or not taken into account on the basis of oversimplified methods. The analogous "Born–Oppenheimer breakdown" invoked (*3*) to explain certain measurements of the dipole moment of HCl and DCl has also been questioned (*6*).

In principle, a somewhat independent check of the validity of this radial function could be achieved if data for $H^{37}Cl$ and $D^{37}Cl$ were available. The nuclear quadrupolar interaction, represented as $q(R)Q$, is the product of the (constant) electric quadrupolar moment Q of a particular nuclide and the gradient of the internal molecular electric field $q(R)$ at that nucleus as a function of the internuclear distance R. Thus although the factor Q differs between ^{35}Cl and ^{37}Cl, the function $q(R)$ is still independent of nuclear mass

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within the Born–Oppenheimer method. Even though the appreciable natural relative abundance of ^{37}Cl in HCl could have made measurements of these expectation values of the nuclear quadrupolar interaction in various vibration–rotational states almost as practicable for H^{37}Cl and D^{37}Cl as for the corresponding isotopic variants containing ^{35}Cl, such measurements have never been reported. In the case of NaBr, however, measurements have been made for both Na^{79}Br and Na^{81}Br (*7*), from which the ratio of the intrinsic electric quadrupolar moments of the ^{79}Br and ^{81}Br nuclides has been estimated (*7, 8*).[1] Pyykko (personal communication) has pointed out that these estimates failed to take into account certain other contributions to this ratio, specifically the second-order magnetic or pseudoquadrupolar effect and the effects due to the nuclear volume and nuclear polarizability. These contributions amount to ~7 ppm for LiBr (*9*), and probably similarly for NaBr.

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J. F. Ogilvie

Academia Sinica
Institute of Atomic and Molecular Sciences
P.O. Box 23-166
Taipei 10764, Taiwan
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[1] The 'electric octupolar moment' referred to in Ref. (*8*) should read 'magnetic octupolar moment.'