

Charge transfer and NQR shift

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nomenon reported in this paper may be of wide occurrence.

A troublesome obstacle to acceptance of our interpretation is that the effective mass along the reaction coordinate should exceed the mass of hydrogen if heavy-atom motion is involved, yet the only good fits to Eq. (1) resulted when $m_H = 1$ and $m_D = 2$ [Eq. (3)], unless one allowed widely different barrier curvatures for the proton and deuterium species. The problem was clarified by fitting to Eq. (1) a set of computed k_H/k_D values (for ethyl chloride plus hydroxide ion, closely similar to recently reported calculations¹²) for which the reaction-coordinate frequencies gave $\nu_H^\ddagger/\nu_D^\ddagger = 1.29$. If $(m_D^\ddagger/m_H^\ddagger)^{1/2} = 1.29$, and $m_D^\ddagger = m_H^\ddagger + 1$, then $m_H^\ddagger = 1.50$ and $m_D^\ddagger = 2.50$. A satisfactory fit to Eq. (1) can be achieved, however, only when $m_H^\ddagger = 1.0$ and $m_D^\ddagger = 2.0$, yet there seems no reason why m of Eq. (3) should not be identified with m^\ddagger of transition state theory.

The source of this paradox may well lie in the assumptions made in the derivation of the Bell tunnel correction. The one-dimensional parabolic barrier is probably an oversimplification, and another possible fault is that a portion of the observed kinetic barrier may involve only solvent reorganization prior to the commencement of proton transfer,¹³ and thus not be available for tunneling. While the Q_H/Q_D values calculated from Eq. (2) in this and other^{6,8} work seem consistent and reasonable, the parameters that go into the calculations (E^H , E^D , a_H , a_D , m_H , and m_D) evidently cannot be interpreted in a precisely literal fashion.

That the paradox may arise from $A_H/A_D < 1$ for reasons other than tunneling was suggested by a referee. Our calculations on models for the E2 reaction give minimum values near 0.9, and other hydrogen-transfer

calculations on tolerably reasonable models suggest a lower limit of 0.7,¹⁴ rather than the 0.5 derived by Bell⁶ for a very unlikely model (transition state bending frequencies near zero). As a test of the referee's hypothesis, we assumed $A_H/A_D = 0.8$ and repeated the fit of the data in 40% DMSO to the Caldin-Mateo program. The tunnel correction was somewhat smaller (1.67 vs 1.82 at 50°), but again the best fit resulted when $m_H = 1.0$ and $m_D = 2.0$.

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NOTES

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The direct connection between nuclear quadrupole coupling constant and charge distribution in a molecule leads to the expectation that the NQR frequency should shift owing to molecular complex formation through charge transfer interaction.¹ Maksyutin *et al.* found a linear relation between ³⁵Cl NQR shift and ionization energy of donor in complexes of picryl chloride with aromatic hydrocarbons.² Although various workers have suggested that it is desirable to extend the measurements to stronger complexes,³ no systematic investigations have been made on strong complexes. Spectro-

photometric investigations have showed that chloranil (tetrachloro-*p*-benzoquinone) forms fairly strong complexes with polynuclear aromatic hydrocarbons.^{4,5} The NQR frequencies of these complexes were measured on a modified superregenerative spectrometer NQR 40 manufactured by Electronic Corporation of India. These measurements showed that there was in fact an approximate linear relation between $\Delta\nu$ (³⁵Cl- μ sec) and energy of the topmost filled π -MO of the hydrocarbons in chloranil-hydrocarbon systems at 295°K (Fig. 1). Owing to crystal field effects quite a number of resonance sig-

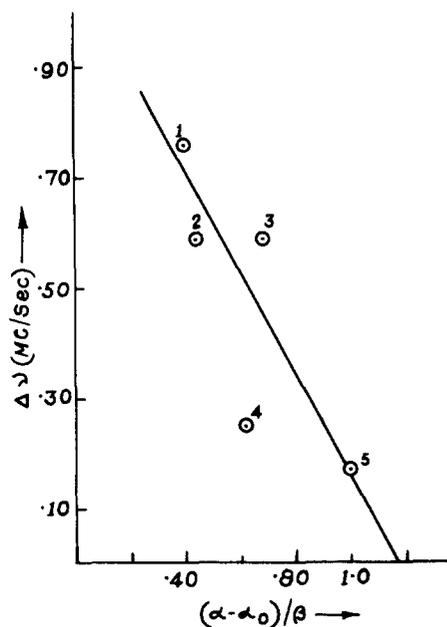


FIG. 1. NQR shift in charge transfer complexes of (1) Anthracene (38.26μ), (2) Pyrene (38.09μ), (3) Triphenylene (38.09μ), (4) Naphthalene (37.75μ), and (5) Benzene (37.67μ) with Chloranil (37.50μ). $(\alpha - \alpha_0)/\beta$ refers to the energy of the highest occupied π -molecular orbital of the hydrocarbon expressed in terms of Coulomb energy α_0 and resonance energy β , in the simple Hückel approximation.

nals are obtained at 77°K , from systems containing chemically equivalent chlorine atoms. At 295°K , however, only one line is obtained. At this temperature the line is less intense and about 0.006μ wide. In these complexes the quadrupolar nucleus (^{35}Cl) was attached to the acceptor molecule. From theoretical consideration Maksyutin *et al.* have shown that if ^{35}Cl be on the donor molecule $\Delta\nu$ should be negative, but they have not given any experimental result in support of their prediction. To test this point NQR frequency of ^{35}Cl was measured with charge transfer complexes of *p*-dichlorobenzene with *s*-trinitrobenzene, picric acid, pyromellitic dianhydride, and tetracyanoquinodimethane. In all these cases $\Delta\nu$ was positive, contrary to theoretical prediction, although a linear relation was obtained be-

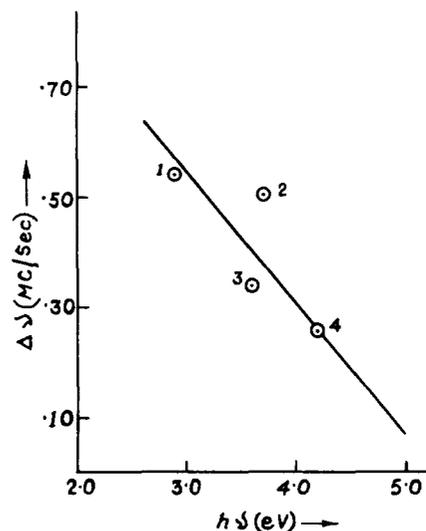


FIG. 2. NQR shift in charge transfer complexes of *p*-dichlorobenzene (34.91μ) with (1) tetracyanoquinodimethane (35.45μ), (2) Picric acid (35.42μ), (3) Pyromellitic dianhydride (32.25μ), and (4) *s*-trinitrobenzene (35.17μ).

tween NQR shift and the charge transfer interaction energy $h\nu$ which is, related to the ionization energy of the donor (I), electron affinity of the acceptor (E), and the ion pair stabilization energy Δ by the Mulliken relation $h\nu_{op} = I - E - \Delta$, and, ν_{op} is the frequency of optical charge transfer transition.

From these results we may conclude that a linear correlation between $\Delta\nu$ and charge transfer interaction energy obtained by optical method do not explain the cause of NQR shift in these molecular complexes, at least not in the way proposed by Maksyutin *et al.*

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