Electron Spin Resonance Spectrum of KrF

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respectively, and evaluated along the imaginary ω axis. They are real along this axis. If $\alpha_{ik}''(\omega)$ and $\beta_{ki}''(\omega)$ are the imaginary parts of the susceptibilities as one approaches the real ω axis from above, then $\alpha_{ik}(i\omega)$ and $\beta_{ki}(i\omega)$ may be written in terms of these functions. Choose α, because the results are the same for β:

$$\alpha_{ik}(i\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\alpha_{ik}''(\bar{\omega})}{\bar{\omega}-i\omega}d\bar{\omega}. \quad (3)$$

We know that α'' may be written in two ways,

$$\int_{-\infty}^{\infty}\frac{\alpha_{ik}''(\omega)}{\pi}e^{i\omega\tau}d\omega = \langle 0 \mid [A_i(\tau), A_k(0)] \mid 0\rangle, \quad (4)$$

and

$$\alpha_{ik}''(\omega) = \pi\sum_m [\langle 0 \mid A_i \mid m\rangle\langle m \mid A_k \mid 0\rangle\delta(\omega-\omega_m)$$
$$- \langle 0 \mid A_k \mid m\rangle\langle m \mid A_i \mid 0\rangle\delta(\omega+\omega_m)], \quad (5)$$

(we choose $\omega_0 = 0$). We average over the ground state of A.

As may be seen from perturbation theory formulas, or equivalently (1) and (3), the average energy approximation is the replacement of ω_m by ϵ_{ik}. This substitution permits closure:

$$\alpha_{ik}''(\omega) = \pi[\langle 0 \mid A_iA_k \mid 0\rangle\delta(\omega-\epsilon_{ik})$$
$$- \langle 0 \mid A_kA_i \mid 0\rangle\delta(\omega+\epsilon_{ik})]. \quad (6)$$

To obtain ϵ_{ik}, simply calculate the first moment of $\alpha_{ik}''(\omega)$, given by

$$\int_{-\infty}^{\infty}\frac{\alpha_{ik}''(\omega)}{\pi}\omega d\omega = \langle 0 \mid \left[i\frac{\partial}{\partial\tau}A_i(\tau), A_k(0)\right] \mid 0\rangle\big|_{\tau=0}$$
$$= \langle 0 \mid [[A_i(0), H_A], A_k(0)] \mid 0\rangle. \quad (7)$$

The susceptibility is odd in ω (and interchange of $k\to i$); the average energy approximation retains this property. Substitute (6) into the left-hand side of (7) and obtain ϵ_{ik}:

$$\epsilon_{ik} = \frac{\langle 0 \mid [[A_i, H_A], A_k] \mid 0\rangle}{\langle 0 \mid [A_i, A_k]_+ \mid 0\rangle}, \quad (8)$$

where $[A_i, A_k]_+$ is an anticommutator. A similar relation holds for B.

It is amusing to look at the third moment (the second moment vanishes) in this approximation:

$$\pi^{-1}\int_{-\infty}^{\infty}\alpha_{ik}''(\omega)\omega^3 d\omega$$
$$= \langle 0 \mid [i^3(\partial/\partial\tau^3)A_i(\tau), A_k(0)] \mid 0\rangle\big|_{\tau=0}$$
$$= \langle 0 \mid [[[[A_i, H_A], H_A], H_A]A_k] \mid 0\rangle. \quad (9)$$

The average energy cubed is

$$(\epsilon_{ik})^3 = \frac{\langle 0 \mid [[[[A_i, H_A], H_A], H_A], A_k] \mid 0\rangle}{\langle 0 \mid [A_i, A_k]_+ \mid 0\rangle}. \quad (10)$$

It is apparent that $(\epsilon_{ik}^3)^{\frac{1}{3}}$ is not necessarily equal to ϵ_{ik}. Note that if we desire to define moments of the ground state as integrals over positive frequencies alone, the second term in (5) does not contribute. Hence we may add and subtract it from the first term multiplied and divided by 2. The even moments now appear with their outermost bracket as an anticommutator.

We conclude that the average energy as it stands can only be of limited usefulness. But one can imagine a variety of iteration schemes in which either the inverse of (4) or the "closed" form of (5) is used.

[1] See, for example, N. Kestner, and O. Sinanoğlu, J. Chem. Phys. 38, 1730 (1963).
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THE trapped radical KrF has been identified in γ-irradiated single crystals of KrF_4. Krypton tetrafluoride was prepared by the low temperature electric discharge method,[1] and single crystals were grown by sublimation between 208° and 195°K. Suitable specimens were isolated, irradiated at 77°K with 1.3-MeV ^{60}Co γ rays, and examined with a Varian V-4502 electron spin resonance (ESR) spectrometer. The irradiated KrF_4 crystals were violet, and an ESR spectrum attributable to KrF was detected in them at 77°K. The radical was stable indefinitely at 77°K, but disappeared on warming a crystal to 120°K.

The ^{19}F $(I=\frac{1}{2})$ hyperfine interaction was measured for KrF radicals in which the krypton isotopes have zero nuclear spin. Unfortunately, ^{83}KrF signals were too weak to be detected (^{83}Kr, abundance 11.6%, $I=\frac{9}{2}$). The KrF_4 crystals were oriented in the magnetic field of the spectrometer so that the spectral parameters could be measured for the "parallel" and "perpendicular" orientations of the Kr–F bond in the radicals. The microwave frequency and the magnetic field of the spectrometer were measured using the same techniques[2] as for the pseudoisoelectronic radical XeF. The principal values of the ^{19}F hyperfine interaction tensor and the g tensor of KrF were determined from

the experimental data with the aid of second-order equations pertaining[2,3] to a single spin one-half nucleus. The experimental data and the results of these calculations are given in Table I.

The isotropic ^{19}F hyperfine interaction $A(F)$ in KrF is 1683 Mc/sec, and is a measure of the spin density in the fluorine $2s$ orbital (neglecting $1s$ polarization). Since $A_0(F)$ is 47 900 Mc/sec for the fluorine $2s$ orbital,[2] the present result indicates a spin population for this orbital of 0.04 in the KrF radical. The anisotropy parameter $B(F)$ of the ^{19}F hyperfine interaction in KrF is 924 Mc/sec indicating $2p$ spin population of 0.61 when compared with the value 1515 Mc/sec estimated[2] for $B_0(F)$.

The radical KrF, being pseudoisoelectronic with XeF, is a σ-electron radical in which the unpaired electron occupies the antibonding σ orbital of the molecule. It was inferred[2] from the spectrum of XeF that this orbital could be adequately described as an out-of-phase combination of Xe $5p_z$ and F $2p_z$ orbitals, their spin populations being 0.36 and 0.47, respectively.

TABLE I. Experimental results[a] and principal values of the ^{19}F hyperfine interaction tensor and g tensor of the radical KrF.

	Parallel	Perpendicular
H^+ (G)[b]	3861	3207
H^- (G)	2597	2939
ν (Mc/sec)[c]	9055.5	9078.1
t (Mc/sec)	3531	759
g	2.000	2.068

[a] Two "near-neighbor" ^{19}F interactions reaching a maximum of 15 and 45 G are ignored.

[b] Error±2 G ($\Delta H_{max.}$ slope 10 G).

[c] Error±0.1 Mc/sec.

It is apparent from a comparison of the present results with those[2] for XeF that the spin population in the F $2s$ and F $2p_z$ orbitals is higher in KrF than in XeF. This observation follows a well-established trend,[4] and is consistent with the higher electronegativity of krypton over xenon, resulting in lower fluorine character in the bonding orbitals of KrF than in those of XeF.

In XeF, $g_\perp$ was 2.1251, considerably greater than the free-spin value of 2.0023. The $\sigma-\pi$ spin–orbit interactions responsible for the positive g shift are clearly less important in KrF.

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Impact Parameter Treatment of Vibrational Excitation

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BOTH the distorted wave approximation[1] (DWA) and the semiclassical impact parameter treatment[2,3] (IPT) have been used to calculate the probability of vibrational excitation in molecular collisions. A one-dimensional model is used, and an exponential interaction is taken between the incoming particle m_3 and the end atom m_2 of a diatomic molecule, m_1-m_2: $W=Ce^{-\alpha x}$. Generally these models have *assumed* that the diagonal matrix elements W_{nn} of the initial j and final n oscillator states are identical[4]:

$$W_{kl}(x) = \langle \phi_k(r) \mid C \exp(-\alpha x + \alpha \gamma r) \mid \phi_l(r) \rangle \equiv Ce^{-\alpha x}V_{kl};$$

however, recent calculations[5] have shown that the DWA results are extremely sensitive to the ratio V_{nn}/V_{jj}. When the anharmonicity of the molecular vibrations is simulated by using Morse oscillators, ratios of 1.01 to 1.5 are obtained and the calculated probabilities are reduced by 10^{-1} to 10^{-2}. The purpose of this note is to show that similar reductions are obtained with the IPT.

The IPT time-dependent perturbation is developed by treating the "averaged" motion of the incident particle by classical mechanics. The incident particle, with reduced mass $\mu_T = m_3(m_1+m_2)/(m_1+m_2+m_3)$ and the mean relative kinetic energy $\bar{\epsilon} = (\epsilon_j + \epsilon_n)/2$ is scattered by the average potential $U(x) = [W_{jj}(x) + W_{nn}(x)]/2 = \bar{V}Ce^{-\alpha x}$. $\bar{V} = \frac{1}{2}(V_{jj} + V_{nn})$. ϵ_j and ϵ_n are the actual initial and final kinetic energies.[6] From the classical solution[2,3] we obtain the time dependence of this potential, $U(t) = \bar{\epsilon} \operatorname{sech}^2(\alpha vt/2)$, where $v^2 = \bar{\epsilon}2/\mu_T$. The interaction may then be represented as $W(t, r) = [U(t)/\bar{V}]e^{\alpha \gamma r}$, and treated by the usual IPT.[7] The probability of undergoing the transition from State j to n with eigenvalues E_j and E_n is given by the following integral:

$$P_{j \to n} = \left(\frac{V_{jn}}{\hbar}\right)^2 \left| \int_{-\infty}^{+\infty} \frac{U(t)}{\bar{V}} \exp\left\{\frac{i}{\hbar} \int_0^t \Gamma_{nj}(t')dt'\right\} dt \right|^2, \quad (1)$$

where $\Gamma_{nj} = E_n - E_j + (V_{nn} - V_{jj})U(t')/\bar{V}$. If the symmetric approximation is made, i.e., $V_{nn} = V_{jj} = 1$, then $\Gamma_{nj} = E_n - E_j$ and Eq. (1) yields the usual result[2,3]:

$$P_{j \to n}^0 = \left(\frac{V_{jn}}{\hbar}\right)^2 \left| 4\bar{\epsilon}\Gamma(1 + iq_0)\Gamma(1 - iq_0)/\alpha v \right|^2$$

$$= \left(\frac{V_{jn}4q_0\pi\bar{\epsilon}}{\alpha v\ \hbar\ \sinh(\pi q_0)}\right)^2,$$

with $q_0 = (E_n - E_j)/\alpha\hbar v$. However, the general integration may be performed by substituting $y = \tanh(\alpha vt/2)$.