Fe–Fe axis. From the spectrum obtained in this orientation, a value of $|D| = 0.15 \pm 0.01 \text{ cm}^{-1}$ is obtained. A large portion of this value of $D$ may be attributed to a direct dipole–dipole interaction:

$$|D|_{\text{dipole–dipole}} = 0.12 \text{ cm}^{-1}.$$

If the magnetic field is rotated 180° in a plane roughly perpendicular to the Fe–Fe axis, two maxima and two minima occur for the inner pair of lines, indicating the necessity for terms in the spin Hamiltonian which are quartic with respect to spin operators. In addition, the antisymmetric exchange interaction, $\mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$, although expected to be small, is allowed by the molecular symmetry.

The resonance lines are not extensively dipolar-broadened even at room temperature most molecules are in the singlet ($S = 0$) ground state. Both the X-band and Q-band linewidths at room temperature are $\sim 150 \text{ G}$ and are reduced at 160°K to $\sim 120 \text{ G}$, a reduction consistent with the removal of intermolecular dipolar broadening by depopulation of thermally excited neighbors.

A broader resonance line having a different temperature dependence is observed for certain orientations at 35.5 GHz. This line is more intense and more anisotropic than those due to the quintet transitions and may be due to the triplet ($S = 1$) state which is expected to have larger zero-field splittings. However, this assignment is not definitely established.

We are indebted to Dr. John Weil of the Argonne National Laboratories for the use of his Q-band spectrometer.

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**On the Jahn-Teller and Pseudo-Jahn-Teller Effect**

**J. S. Alper and R. Silbey†**

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The Jahn-Teller and pseudo-Jahn-Teller effects involving degenerate and nearly degenerate electronic levels, respectively, have been of interest for a number of years.1–3 The work of Longuet-Higgins et al.1 is the most complete numerical study of this effect for the case of a doubly degenerate vibrational mode interacting with a doubly degenerate electronic level. These authors diagonalized the relevant matrices by computer. Hobey4 has derived an elegant iterative method to solve the coupled equations. We present a new systematic study of the energy lowering in the Jahn-Teller effect.

**Table I.** Energy lowering in Jahn-Teller effect (in units of $\omega$).

<table>
<thead>
<tr>
<th>$\delta^2$</th>
<th>Ref. (1)</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>−0.226</td>
<td>−0.223</td>
</tr>
<tr>
<td>0.5</td>
<td>−0.422</td>
<td>−0.408</td>
</tr>
<tr>
<td>1.0</td>
<td>−0.767</td>
<td>−0.716</td>
</tr>
<tr>
<td>2.0</td>
<td>−1.369</td>
<td>−1.245</td>
</tr>
<tr>
<td>5.0</td>
<td>−2.961</td>
<td>−2.790</td>
</tr>
<tr>
<td>20.0</td>
<td>−10.493</td>
<td>−10.250</td>
</tr>
</tbody>
</table>

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6. Present work.
Teller effect.

The coupling has been taken to be linear in the coordinate method which requires relatively little computation and which gives excellent agreement with the work of Ref. 1. We have also applied the method to the pseudo-Jahn-Teller effect.\(^3,4\)

The Hamiltonian for this problem may be written in second quantized form as

\[
H = \epsilon(c_a^+c_a + c_b^+c_b) + \omega(b_1^+b_1 + b_{-1}^+b_{-1}) + k\omega(c_a^+c_b^+b_1^+b_{-1}) + c_M(c_a^+c_b^+b_{-1}^+b_1),
\]

where the \(c_a\) and \(c_b\) are the annihilation operators for an electron in the degenerate \(\alpha\) and \(\beta\) orbitals of energy \(\epsilon\); the \(b_1\) and \(b_{-1}\) are the annihilation operators for quanta of vibrations \(l\) and \(-l\), respectively, each of energy \(\omega\). The coupling has been taken to be linear in the coordinate. We have used the complex orbitals \(\alpha\) and \(\beta\), and the complex vibrational coordinates \(l\) and \(-l\) in accord with previous work. However, it is more convenient to use the real orbitals and coordinates defined by the transformations

\[
b_1 = \sqrt{2}(b_1 + b_{-1}) ; \quad b_2 = (\sqrt{2}i)(b_1 - b_{-1}),
\]

\[
c_1 = \sqrt{2}(c_a + c_b); \quad c_2 = (\sqrt{2}i)(c_a - c_b).
\]

Using these we find

\[
H = \epsilon(c_1^+c_1 + c_2^+c_2) + \omega(b_1^+b_1 + b_{-1}^+b_{-1}) + (k\omega)/(\sqrt{2})
\]

\[
\times [c_1^+c_1 c_2^+c_2 (b_1 + b_{-1}) - (c_1^+c_1 + c_2^+c_2) (b_1 + b_{-1})].
\]

We may remove the first coupling term by performing a unitary transformation on \(H\). The transformed Hamiltonian is given by \(\tilde{H} = U^+HU\), with

\[
U = \exp[(k\omega)/(\sqrt{2}) (c_1^+c_1 - c_2^+c_2) (b_1 - b_{-1})].
\]

Thus

\[
\tilde{H} = \epsilon(c_1^+c_1 + c_2^+c_2) + \omega(b_1^+b_1 + b_{-1}^+b_{-1})
\]

\[
- \frac{k\omega}{2}[c_1^+c_1 (c_2 + c_2^+)(b_1 + b_{-1})^2 - (k\omega)/(\sqrt{2}) (b_1^+b_1 + b_{-1}^+b_{-1})]
\]

\[
\times [c_2^+c_2 \exp[-\sqrt{2}k(b_1 - b_{-1})] + c_1^+c_1 \exp[\sqrt{2}k(b_1 - b_{-1})]].
\]

Notice that the third term in \(\tilde{H}\) is already diagonal. We now calculate the energy of the ground state, \(c_1^+|0\rangle\), (where \(|0\rangle\) is the vacuum state) to second order in the nondiagonal term of \(\tilde{H}\). We find

\[
\Delta E = -\omega(\frac{1}{4}k^2 + \frac{1}{4}\epsilon^2)(1 - \exp(-2k^2)).
\]

In Table I we compare this energy lowering to the energy of the lowest state of Ref. 1 for a large range of \(k\). The agreement is excellent.

We have also calculated the electronic energy splitting for the pseudo-Jahn-Teller effect by the same method. We first add a term \(\frac{1}{2}\Delta E (c_1 c_1 - c_2 c_2)\) to \(\tilde{H}\). The initial energy splitting \(\Delta E\) is changed to \(\Delta W\) due to the vibronic interaction. Using the values of \(\Delta E\) and \(k\) given by Hobey\(^3\) or Purins and Karplus\(^4\) we have calculated \(\Delta W\) (again to second order). The results are given in Table II. The agreement is again excellent.

A more detailed discussion of this work will be published at a later date.

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† Alfred P. Sloan Foundation Fellow.

### Table II. Energy splitting in pseudo-Jahn-Teller effect.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta E) (Present work)</th>
<th>(\Delta W) (Previous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene-</td>
<td>708 cm(^{-1})</td>
<td>483 cm(^{-1})</td>
</tr>
<tr>
<td>Toluene-</td>
<td>548(^b)</td>
<td>390 cm(^{-1})</td>
</tr>
<tr>
<td>Toluene-</td>
<td>365(^b)</td>
<td>267 cm(^{-1})</td>
</tr>
</tbody>
</table>

\(^a\) Reference 3.
\(^b\) Reference 4.

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### Fluorescence Decay Times of Photoexcited Benzene and Toluene in the Gas Phase

**George M. Breuer† and Edward K. C. Lee**

Department of Chemistry, University of California, Irvine, California 92664

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Fluorescence decay times in the nanosecond region have been measured through a pulse sampling or a phase-shift technique in recent years.\(^1\) Most measurements have been made in condensed media,\(^1,2\) avoiding problems with low intensity in the gas phase. Since gas-phase data are needed in the assessment of the competition between radiative and radiationless processes, we wish to report preliminary results obtained on the decay times of the first excited singlets of benzene and toluene in the gas phase.

A pulsed deuterium discharge lamp (TRW nanosecond spectral source 31A, 4–7-nsec pulse at half-peak width) with saturated CoSO\(_4\)/NiSO\(_4\) and “DaP” solution filters\(^6\) (transmission between 230 and 280 nm, 58% at 252 nm) was used for excitation most frequently. Fluorescence intensity from the sample in a gas cell at room temperature was monitored by a photomultiplier tube (RCA 1P28 or 8575 V1) whose output was sampled and displayed on an oscilloscope (Tektronix 556 with lSl plug-in). The displays were photographed and averaged over 10 or more displays to improve the signal-to-noise ratio.