\[ \Delta E_{\text{as}} / \Delta E_{\text{tot}} \] For example, if asymmetric stretching gives up \( \Delta E_{\text{as}} \), bending-symmetric stretching gains \( \Delta E_{\text{bs}} \) with \( \Delta E_{\text{as}} = G \Delta E_{\text{bs}} \). For \( G \) less than unity, translation-rotation then also gains energy; for \( G \) greater than unity it loses some to bending-symmetric stretching.

By the use of considerations from irreversible thermodynamics,\(^4\) phenomenological rate equations for small departures from equilibrium can be derived:

\[
dE_{\text{as}} / dt \mid_{\text{eq}} = (\tau_{\text{VV}})^{-1} (\epsilon_{\text{as}} - \epsilon_{\text{as}}) + (\tau_{\text{VV}})^{-1}
\times [G^2(\epsilon_{\text{as}}/\epsilon_{\text{as}} - \epsilon_{\text{as}}) - G(\epsilon_{\text{as}}/\epsilon_{\text{as}} - \epsilon_{\text{as}})] \
\]

\[
dE_{\text{bs}} / dt \mid_{\text{eq}} = (\tau_{\text{VV}})^{-1} [G(\epsilon_{\text{bs}}/\epsilon_{\text{bs}} - \epsilon_{\text{bs}}) - G(\epsilon_{\text{bs}}/\epsilon_{\text{bs}} - \epsilon_{\text{bs}})] \
\]

\[ (\tau_{\text{VV}}) \]

The relaxation times \( \tau_{\text{VV}} \) and \( \tau_{\text{bb}} \) are for the V-V and V-V interactions, respectively; \( (\epsilon_{\text{as}} - \epsilon_{\text{as}}) \) is the difference between the energy per unit mass that a mode would have were it in equilibrium with translation and what it actually has; \( \epsilon_{\text{bs}} \) is the specific heat per unit mass for the given mode. The subscript \( (\cdot) \) refers to bending-symmetric stretching, and \( (\cdot) \) to asymmetric stretching. For specific cases these equations can be derived from microscopic considerations as outlined by Herzfeld and Litovitz.\(^5\)

Application of the above equations to a spectrophone in which asymmetric stretching is radiatively excited gives for the phase lag \( \psi \) due to vibrational nonequilibrium

\[
\tan \psi = \frac{(G+K_{G}-1)\omega_{\text{VV}} + (\epsilon_{\text{tot}}/\epsilon_{\text{tot}})\omega_{\text{VV}} + (\epsilon_{\text{tot}}/\epsilon_{\text{tot}})(1-G)\omega_{\text{TT}}}{1 + \omega_{\text{VT}}((1-G)K_{G}\omega_{\text{VT}} + (1-G)(\epsilon_{\text{tot}}/\epsilon_{\text{tot}}) - (\epsilon_{\text{tot}}/\epsilon_{\text{tot}})\omega_{\text{VV}})}, \tag{3}
\]

which implies the exchange of three bending-mode quanta (or one bending and one symmetric stretching) for one asymmetric-stretching quantum.

Before final conclusions about a dominant V-V transition can be made, the experimental data must be more precise; it is equally important to use theoretically complete equations to interpret the data.


7. See Ref. 1.


**Differential Elastic Scattering of D₂ by N₂ in Crossed Molecular Beams**

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Until recently, high-resolution measurements of elastic differential scattering cross sections were limited to systems containing an alkali atom because of the
inherently low efficiency of electron-bombardment molecular beam detectors usually used for nonalkali systems. We have measured the nonreactive differential scattering of $D_2$ by $N_2$ and have observed quantum-mechanical rapid interference oscillations from 2 to 20 deg c.m. These oscillations were visible despite the fact that the experimental cross sections are averages over the rotational quantum states, relative energy distribution, scattering volume, and detector acceptance angle. The extrema positions were fitted by a theoretical calculation assuming a spherically symmetric potential, and the position $r_0$ of the potential zero was determined.

An early version of the apparatus has been described elsewhere. A modulated, aerodynamically intensified (nozzle) $D_2$ primary beam crossed an $N_2$ nozzle beam at 90 deg. The density of the scattered $D_2$ was measured by a differentially pumped quadrupole mass spectrometer which was rotated about the scattering center in the plane of the two beams. The signals were integrated for up to 2 h by using a strip-chart recorder and a 100-sec lock-in amplifier time constant. The $D_2$ and $N_2$ beams had a full width at half-maximum (fwhm) of 0.6 and 7 deg, respectively, and the scattering volume was about 30 mm$^3$. The width of the circular detector entrance was 1.6 deg. The Mach number of the $D_2$ beam, measured by a slotted-disk velocity selector, was 9; the estimated Mach number of the $N_2$ beam was 6. The most probable relative kinetic energy $E$ was 0.069 eV (1.1$\times$10$^{-13}$ erg).

The points shown in Fig. 1 (a) are the experimental cross sections, converted to the c.m. coordinate system, multiplied by the sine of the c.m. scattering angle $x$. The cross sections, each divided by the value determined from a least-squares straight-line fit to a log-log plot of cross section vs $x$, are shown in Fig. 1 (b). Eight extrema are clearly resolved.
Notes

Electron Spin Resonance Study of Transition Elements in Strontium Tartrate and Calcium Tartrate*

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We have observed the electron spin resonance (ESR) spectra of several transition element ions in single crystals of calcium tartrate tetrahydrate (CaTr) and strontium tartrate tetrahydrate (SrTr). The crystals are grown in silica gel with a few percent of the dopant apparently entering substitutionally. The crystals are orthorhombic and have the P2₁2₁2₁ space group with four nonequivalent molecules per unit cell. Room temperature ESR spectra of single crystals of CaTr:Cu showed many similarities to the SrTr:Cu system. Four nonequivalent sites for the Cu²⁺ ion and the same symmetry directions and planes were present. To bypass the multiple site problem, the spin-Hamiltonian parameters were obtained from powder spectra. The lines of an ESR powder spectrum usually give directly the components of the g tensor and the hyperfine splitting (hfs) tensor. X-band ESR powder spectra of SrTr:Cu at 300 and 100°K are shown in Figs. 1(a) and 1(b), respectively. Cu²⁺ hfs is observable along all principal axes in the better resolved 100°K spectrum. The ⁶⁵Cu and ⁶⁴Cu isotope splitting is also resolved. Comparison of this spectrum with a KU-band powder spectrum at 100°K clearly distinguished between g values and hfs contributions to the overlapping lines and allowed the determination of all the spin-Hamiltonian parameters. The results for CaTr:Cu and SrTr:Cu are listed in Table I.

In both systems, gzz decreases and Azz increases with decreasing temperature; however, there is little change below 100°K. Furthermore, there is a second Cu²⁺ resonance with slightly different temperature-independent hfs splittings in CaTr. Dehydration effects indicate that the Cu²⁺ hfs may depend on the number of H₂O molecules near the ion. No similar "second" resonance was observed in the SrTr:Cu system. Evidence for an additional z direction was also observed in the CaTr: Mn system by Wakim.

The ESR spectrum of SrTr: Mn consists of 120 main lines plus "forbidden" transitions, the expected result for Mn³⁺ (S = ⁵/₂, I = ⁷/₂) ions in four nonequivalent sites. The symmetry planes and axes are the same as in SrTr:Cu. The angles which the z component of the g tensor makes with the crystallographic axes are essentially the same as those found by Wakim et al. for CaTr: Mn. The parameters of the spin Hamiltonian containing the cubic fourth-order spin terms were obtained from a least-squares fit of the data using a computer program written by Swalen and Gladney and are listed in Table I. The large uncertainty in K is due to the uncertainty in the Euler angle, ψ, which could not be determined accurately due to the multiple sites.

Preliminary studies of SrTr: Ni, SrTr: V, and SrTr: Co were also made. ESR lines due to Ni²⁺ were not observed, even at 4.2°K, presumably due to a very large

### Table I. Spin-Hamiltonian parameters of SrTr:Cu, CaTr:Cu, and SrTr:Mn.

<table>
<thead>
<tr>
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<th>SrTr:Cu</th>
<th>CaTr:Cu</th>
<th>SrTr:Mn</th>
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</thead>
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<tr>
<td>gxx</td>
<td>2.115±0.002</td>
<td>2.061±0.002</td>
<td>0.002±0.002</td>
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<tr>
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<td>2.111±0.002</td>
<td>0.002±0.002</td>
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<tr>
<td>gx</td>
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<td>2.406±0.001</td>
<td>0.002±0.002</td>
</tr>
<tr>
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<td>23 G±2 G</td>
<td>8 G±1 G</td>
</tr>
<tr>
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<td>27 G±2 G</td>
<td>21 G±2 G</td>
<td>-102 G±1 G</td>
</tr>
<tr>
<td>Axx</td>
<td>109 G±1 G</td>
<td>107 G±1 G</td>
<td>-94 G±1 G</td>
</tr>
</tbody>
</table>

Fig. 1. (a) Room temperature ESR powder spectrum of copper-doped strontium tartrate at 9.285 GHz. (b) The same sample at 100°K.