Jahn-Teller Effect in Liquids: General Principles and a Molecular-Dynamics Simulation of the Cupric Ion in Water

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We discuss the general conditions under which a Jahn-Teller effect can be meaningfully associated with the solvation shell of an ion in solution. Unlike the Jahn-Teller effect in solids, no distortion of the solvation shell exists on the longest time scales. On intermediate time scales, the solvation shell exhibits cubic (O_h) symmetry and on the shortest scales it shows the Jahn-Teller distortion (D_{4h}) . A moleculardynamics simulation of a model in which the frame of reference for the Jahn-Teller potential rotates in time exhibits these features and shows how the time scales involved vary with parameters in the potential.

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The Jahn-Teller effect is well known in solids [1]. It is also known that there is an analogous effect when, for example, strongly solvated transition metal cations are dissolved in polar liquids. In the case of cupric ion in water, neutron scattering evidence [2] was reported of the expected E_g type of distortion of the six octahedrally coordinated water molecules which solvate the ion. Earlier extended x-ray-absorption fine structure and x-ray experiments [3-5] also showed evidence of the effect. On the theoretical side, there are some electronic structure calculations of the expected distortion for a fixed orientation of the six water molecules surrounding the cation [6]. A full understanding of the meaning of the Jahn-Teller effect in liquids poses some conceptual problems however.

We discuss the cupric ion in water, on which we have made the calculation reported below; but it should be clear that the considerations have greater generality. Many divalent ions attract six water molecules to nearest-neighbor positions around the ion in an approximately octahedral configuration (Fig. 1). For ions such as Cu^{++} which exhibit the Jahn-Teller effect in solids one expects that the octahedron (symmetry O_h) will distort to

 $\begin{array}{c} & Z \\ & 3 \\ & Y \\ & 2 \\ & 4 \\ & & 1 \\ & & 5 \\ & & 6 \end{array}$

FIG. 1. The octahedral configuration of ligands (here oxygen atoms) around an ion with definitions of coordinate labels.

a configuration with D_{4h} symmetry at the ion site. [We ignore the hydrogens on the water molecules in this discussion. Usually they will undergo librations on a time scale faster than all the time scales (except τ_{vib}) which we discuss here, so that they will not modify the arguments made below.] On the other hand, in a liquid, over the longest times of interest here ($\tau_{rot} \approx 10^{-10}$ sec), the distorted octahedron will rotate, so that the average positions of the oxygen atoms around the copper will have a rotationally invariant distribution (as observed, for example, in the copper-oxygen pair distribution function). The breaking of this rotational symmetry is seen only if we consider average positions over time scales much less than the average rotation time τ_{rot} of the solvation shell. This condition is sufficient to assure observation of breaking of rotational symmetry, but not necessarily of the cubic (O_h) symmetry unless a further condition is met: There are three equivalent D_{4h} distortions (Fig. 2) and, in a



FIG. 2. Three equivalent D_{4h} distortions of the octahedral configuration of Fig. 1.

liquid, transitions can occur between them, say, at a rate $1/\tau_{hop}$. If the coordinate positions of the oxygen atoms are averaged over times less than τ_{rot} but much larger than τ_{hop} then a shell of O_h , not D_{4h} , symmetry will be seen.

In summary, let the time over which the coordinate positions of the oxygen atoms of the solvation shell is averaged be T_{av} . The averaged positions of the solvation shell will exhibit the following point group symmetries with respect to the position of the cupric ion under various averaging conditions: $T_{av} \gg \tau_{rot}$, full rotation group [O(3)] symmetry; $\tau_{hop} \ll T_{av} \ll \tau_{rot}$, O_h symmetry; $\tau_{vib} \ll T_{av} \ll \tau_{hop}$, D_{4h} symmetry, where in the last set of inequalities we define a time scale τ_{vib} characterizing the period of the harmonic vibrations of the solvation shell. Thus, the Jahn-Teller effect in liquids should be understood as a kind of dynamical symmetry breaking which is only manifested on short time scales and is progressively "washed out" on longer time scales.

For the case of the hydrated cupric ion, a characterization of the solid state Jahn-Teller effect is given [7] by

$$H_0 + H_{\rm JT} \,, \tag{1}$$

in which the distortion is produced by the second term which takes the form, for an octahedrally coordinated ion,

$$H_{\rm JT} = A_1 (Q_\Theta \sigma_Z - Q_\epsilon \sigma_X) + A_2 [(Q_\Theta^2 - Q_\epsilon^2) \sigma_Z + 2Q_\Theta Q_\epsilon].$$
(2)

Here the atomic coordinates Q_{Θ} and Q_{ϵ} are defined as

$$Q_{\Theta} = \left(\frac{m\omega_{E_g}}{24\hbar}\right)^{1/2} [2(z_3 - z_6) - (x_1 - x_4) - (y_2 - y_5)],$$
(3)

$$Q_{\epsilon} = \left(\frac{m\omega_{E_{\epsilon}}}{4\hbar}\right)^{1/2} \left[(x_1 - x_4) + (y_2 - y_5) \right].$$
(4)

 ω_{E_g} is the harmonic frequency of the E_g mode of the solvation shell in the undistorted state and *m* is the mass of the ligand (here oxygen). The Pauli matrices operate on spinors which describe the electronic state of the cupric ion. The spinor $\binom{0}{1}$ is the state in which the hole in the *d* shell lies on one of the two degenerate e_g orbitals while the spinor $\binom{1}{0}$ is the state in which the hole in the *d* shell lies in the other e_g orbital.

The coordinate system in (3) and (4) is defined with respect to six octahedrally coordinated oxygen atoms (in water molecules) surrounding the copper ion as shown in Fig. 1. The reference frame for this coordinate system is obviously the crystal axes in the solid state Jahn-Teller effect. In the liquid state, it is less obvious what reference frame should be used. If a fixed coordinate system were used, then the coordinates Q_{Θ} and Q_{ϵ} would become very large as the time became comparable to a rotational diffusion time τ_{rot} because the oxygen atoms would not be

near the axes of the fixed coordinate system. Then the expansion implicit in (2) would become invalid. On the other hand, if we define a coordinate reference frame with respect to the instantaneous positions of the solvating atoms, then the coordinate system itself will have dynamics on the same time scale as the dynamics generated by the Hamiltonian (2). A reference frame where (2) is meaningful and valid is one which is determined by the average positions of the solvating entities (here oxygen atoms), where the average is made over a time T_{av} large compared to characteristic vibrational time scale τ_{vib} , but small compared to characteristic rotational diffusion times τ_{rot} . If such a time scale does not exist, then the Jahn-Teller effect in liquids is not a well-defined concept. Assuming that T_{av} exists we define a reference frame as follows. Let the instantaneous positions of the solvation shell oxygen nuclei be $\{\mathbf{r}_i(t_n)\}$, i = 1, ..., 6 at time t_n . Designate time at a discrete set of time "steps" of duration Δt . Let $N_{av} = T_{av} / \Delta t$ and define average solvent shell atom positions $\{\overline{\mathbf{r}}_i(t_n)\}$ by

$$\overline{\mathbf{r}}_{i}(t_{n}) = \frac{1}{N_{\text{av}}} \sum_{n'=1}^{N_{\text{av}}} \mathbf{r}_{i}(t_{n} - n'\Delta t) .$$
(5)

Then define unit vectors

$$\mathbf{u}_{1}(t_{n}) = \frac{\overline{\mathbf{r}}_{1}(t_{n})}{|\overline{\mathbf{r}}_{1}(t_{n})|}, \qquad (6)$$

$$\mathbf{u}_{3}(t_{n}) = \frac{\overline{\mathbf{r}}_{1}(t_{n}) \times \overline{\mathbf{r}}_{2}(t_{n})}{\left|\overline{\mathbf{r}}_{1}(t_{n}) \times \overline{\mathbf{r}}_{2}(t_{n})\right|},\tag{7}$$

$$\mathbf{u}_2(t_n) = \mathbf{u}_3(t_n) \times \mathbf{u}_1(t_n) . \tag{8}$$

These define directions of the axes of a coordinate system where Q_{Θ} and Q_{ϵ} can be obtained from (3) and (4). (Other similar definitions will work as well. Differences between this and other natural choices are very small if the averaging time is as indicated.) This coordinate system rotates diffusively as the solvation shell rotates in the solution. This time-dependent rotation of the frame of reference for (2) in our simulations distinguishes the phenomenon discussed here from the solid state Jahn-Teller effect. As a result of the rotation, our calculations show the dynamical Jahn-Teller symmetry breaking discussed qualitatively above.

To obtain an explicit molecular-dynamics model, we suppose that Eq. (2) can be treated adiabatically, diagonalize (2) with respect to the electronic degrees of freedom, and suppose that the system moves only on the lower-energy surface given by

$$H_{ad} = H_0 - \{ [A_1 Q_{\Theta} + A_2 (Q_{\Theta}^2 - Q_{\epsilon}^2)]^2 + (A_1 Q_{\epsilon} - 2A_2 Q_{\Theta} Q_{\epsilon})^2 \}^{1/2}.$$
(9)

This gives a classical model [8] which may be simulated by standard molecular-dynamics techniques. The only peculiar feature is that we must calculate the running average orientation of the coordinate system [Eqs. (5) and (6)-(8)] during the molecular-dynamics run in order to define the coordinates Q_{Θ} and Q_{ϵ} and hence to calculate the forces which lead to the distortion of the solvation shell using the last equation.

We used a molecular-dynamics model of 216 molecules of water and one "copper" ion. The water model is the Toukan-Rahman model [9]. The simulations are done at fixed volume in a microcanonical ensemble with an average kinetic energy corresponding to a temperature of 300 K. The cubic box has periodic boundary conditions and Coulomb interactions are treated by standard Ewald techniques. The model gives a good account of many of the experimental properties of water. The cupric ion was assigned a charge of +2. The short-range part of the two-body "copper"-oxygen potential was [10]

$$V_{\rm Cu-O} = Ae^{-Br} - \frac{C}{r^4} - \frac{D}{r^6} - \frac{F}{r^{12}}, \qquad (10)$$

where A-F are parameters obtained from an *ab initio* molecular orbital calculation of the cupric-ion-water potential. The potential is qualitatively reasonable and leads to a coordination number of 6 in the first solvation shell in the simulation. (Many-body effects [11-13] which we do not include here may be important for a complete description.) The values of A-F used in our simulations are A = 79.63 hartree = 150.48 $e^2/Å$, B = 1.919 bohr⁻¹= 3.6260 Å⁻¹, C = 27.49 hartree bohr⁴ = 4.0734 $e^2 Å^3$, D = -104.25 hartree bohr⁶ = -4.3277 $e^2 Å^5$, and F = 1441 hartree bohr¹² = 1.3130 $e^2 Å^{11}$. (The resulting potential well for a water-copper-ion pair has a depth of about 4.32 eV which occurs at 1.90 Å.) With a time step of $\Delta t = 0.4 \times 10^{-15}$ sec, the value $N_{av} = 600$ fulfilled the stated conditions for the averaging process in Eq. (5). We report results using several values of the parameters A_1 and A_2 .



FIG. 3. Constant potential contours of the parts of the potential in H_{ad} which depend only on interactions between the seven atoms comprising the ion and its nearest-neighbor solvation shell. Here $X_{\Theta} = (2\hbar/m\omega_{E_g})^{1/2}Q_{\Theta}$ and $Y_{\epsilon} = (4\hbar/m\omega_{E_g})^{1/2}Q_{\epsilon}$.

Figure 3 shows potential contours of the part of the potential in the Hamiltonian which depends on the coordinates Q_{ϵ} and Q_{Θ} . The three minima marked M_1, M_2, M_3 correspond respectively to the three distortions shown in Fig. 2. They are separated by saddle points S_1 , S_2 , and



FIG. 4. System point contours for three choices of the parameters A_1 and A_2 in the Jahn-Teller potential function. (a) Strong Jahn-Teller potential; $A_1 = 3560 \text{ cm}^{-1}$, $A_2 = 108 \text{ cm}^{-1}$. (b) Intermediate Jahn-Teller potential; $A_1 = 904 \text{ cm}^{-1}$, $A_2 = 83 \text{ cm}^{-1}$. (c) Weak Jahn-Teller potential; $A_1 = 822 \text{ cm}^{-1}$, $A_2 = 27.5 \text{ cm}^{-1}$.

 S_3 . The process of passing from one of the minima to another by passage over (or near) the saddle point is the process characterized by the time τ_{hop} . At the origin in this plane the potential surface touches the second, higher-energy potential surface generated by diagonalizing the Hamiltonian (2) with respect to electronic coordinates. We find that the adiabatic approximation is well satisfied because the separation of the two surfaces is much larger than k_BT at all points on the lower surface visited by the system point.

Figure 4 shows system trajectories projected onto the Q_{ϵ} - Q_{Θ} plane for three different choices of the parameters A_1 and A_2 as given in the figure caption. All these parametrizations give distortions of the octahedral shell which are in order-of-magnitude agreement with (widely scattered) experimental reports. The parameters are chosen so that $\tau_{hop} \gg \tau_{vib}$, $\tau_{hop} > \tau_{vib}$, and $\tau_{hop} \approx \tau_{vib}$, respectively. In the first case, the solvation shell falls into one of the three possible distortions and stays there (though the shell is rotating). In the second case one sees occasional transitions from one distortion to another. In the third case, the solvation shell spends almost as much time passing between distortions as it does in any one of them. Our estimates of the parameters A_1 and A_2 from crystal data and ab initio calculations suggest that the behavior of the real cupric ion most closely resembles the last case, in which the solvation shell spends much of its time between distortions.

In conclusion, we have clarified the sense in which the Jahn-Teller effect can be meaningfully discussed in a liquid, where the attendant symmetry breaking can only be a dynamical effect and we have realized the resulting picture in a molecular-dynamics simulation of the cupric ion in water. This formulation opens the way to study many interesting effects associated with Jahn-Teller distortions of solvation shells of ions in polar liquids. These include the study of the rates of the isomeric transitions from one distortion to another, the consequences for Raman, infrared, and other vibrational spectroscopies, the expected signatures of the distortions in various experimental probes which explore the solvation shell on

different time scales, and the implications of the Jahn-Teller effects on electron transfer rates.

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