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Manifestation of Chaotic Nuclear Dynamics of Highly Excited Polyatomic Molecules in Time-Resolved Electron Diffraction Data

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The effects of chaotic nuclear motion on time-resolved electron diffraction data recorded of vibrationally highly excited polyatomic molecules are investigated. For this purpose the time-dependent scattering intensities are expressed directly in terms of the joint phase space probability density in the form of the Wigner function. A simple semiclassical procedure is described that allows one to obtain the scattering intensities for polyatomic molecules in a state of chaotic nuclear motion using internuclear pair potentials. Model calculations show that electron diffraction intensities of molecules in a state of chaotic motion are clearly different from intensities obtained for systems in a state of regular nuclear motion. The procedure was applied to analyze electron diffraction data of sulfur hexafluoride, SF_6, recorded in the temperature range from 650 K, the spectroscopically determined beginning of the quasi-continuum, up to 773 K. The analysis shows that, in this temperature range, the molecule exists in a state of regular nuclear motion. This result is remarkable because it indicates that the appearance of the quasi-continuum does not necessarily indicate the onset of chaotic nuclear motion.

Introduction

With the extension of electron diffraction to studies of time-dependent molecular phenomena, such as coherent nuclear dynamics in laser-excited molecules,[1−7] wave packet evolution,[7] or photodissociation and predissociation processes,[1−7] it has become necessary to develop theoretical expressions for electron diffraction intensities that depend on other than equilibrium-state distributions in molecular ensembles.

Time-resolved electron diffraction (TRED)[1,2] is essentially an integrative technique that provides time-averaged observations of an evolving ensemble of molecular states resulting, for example, from the effects of a laser field. Nevertheless, despite the integral nature of the data, it is possible to extract from them detailed information on state distributions in molecular ensembles because, by applying stochastic techniques of data analysis,[1,8] one can determine time-averaged position probability density functions. From the latter the density matrix[9,10] of a prepared molecular quantum state or a joint phase-space probability density function, such as the Wigner function,[11,12] can be reconstructed,[13] using the so-called quantum sampling technique of Leonhardt et al.[14−17] or of Wünsche and Richter.[18,19]

A related area of study, one that has found considerable interest for more than two decades (see, e.g., refs 20−23), concerns the ability of molecular quantum systems to respond to some time-dependent external excitation by changing from a state of regular nuclear dynamics to one of chaotic motion. So far, studies of the onset of quantum chaos have typically been based on observations of the statistics of spectra[20,24,25] or the statistics of energy level spacing.[23] Recently, Wilkie and Brumer[26] have described how a statistically significant temporal signature of quantum chaos can be extracted from the fluorescense decay of mixed molecular states prepared by multimode partially coherent laser pulses.

It is the purpose of the current paper to describe a nonoptical time-dependent technique suited for studying chaotic molecular dynamics. Specifically, we want to describe the manifestation of such chaotic behavior in TRED intensities of highly vibrationally excited polyatomic molecules.

Theory

1. Molecular Intensity Function. TRED data of polyatomic molecules vibrationally excited above the critical energy, E_c,[27−29] which leads to the onset of chaotic nuclear motion, must be expected to be different compared with such data recorded from systems with the same characteristic energy, but in a hypothetical state of regular nuclear motion. This view is suggested by wave function calculations[21] which illustrate the specific evolution of the transition from regular to chaotic behavior. That is, in the domain of regular motion, the wave functions are highly localized in some region of state space, whereas they begin to diffuse at the onset of chaotic behavior.[21] Since TRED intensities are functions of the position-dependent probability density, $P(r,t)$, they reflect directly the features associated with this change of state. The time-dependent molecular electron diffraction intensities, $M(s,t)$, can be expressed in the following way:[1,7,8]

$$M(s,t) = (I_0/R^2)g(s) \int P(r,t) \exp(i\mathbf{sr})\, dr \qquad (1)$$

where $s = |\mathbf{s}| = 2|\mathbf{k}| \sin(\vartheta/2)$, $\mathbf{k}$ is the momentum vector of the scattered electrons, ϑ is the scattering angle, I_0 is the incident electron beam profile, R is the scattering distance, $g(s)$ represents the scattering functions,[30] and $\mathbf{sr}$ is the dot product of the scattering vector $\mathbf{s}$ and the internuclear pairwise distance vector

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$\mathbf{r}$. Integration in eq1 and in the following equations is over the infinite space, if not indicated otherwise.

In eq 1, $P(r,t) = |\Psi(r,t)|^2$. Evaluating the wave functions $\Psi(r,t)$ for highly excited polyatomic systems is a difficult problem, which precludes direct calculations of $P(r,t)$ in most cases. However, with some adequate assumptions, it is possible to evaluate the joint phase-space probability density, e.g., the Wigner function.[11,12] The Wigner function, $W(p,r)$, can be determined[11,12] by the equation

$$W(p,r) = (1/\pi\hbar)\int \exp(2ipx/\hbar)\langle r - x|\boldsymbol{\rho}|r + x\rangle\, dx \qquad (2)$$

where $\boldsymbol{\rho}$ is the density matrix[9,10] and p is the momentum.

Considering the marginal property[12] of $W(p,r)$

$$P(r,t) = |\Psi(r,t)|^2 = \int W(r,p,t)\, dp \qquad (3)$$

eq 1 can be written

$$M(s,t) = (I_0/R^2)g(s)\ \mathcal{R}e\{\int dp \int dr\ W(r,p,t)\langle \exp(i\mathbf{sr})\rangle_{\mathbf{sp}}\} \qquad (4)$$

where $\mathcal{R}e\{...\}$ denotes the real part and the brackets $\langle ...\rangle_{\mathbf{sp}}$ signify spatial averaging over the molecular ensemble.

Equation 4 is the most general representation of TRED molecular intensities in terms of the Wigner function. In this representation $M(s,t)$ can be interpreted as the filtered projection of the Wigner function, with the scattering operator $\exp(i\mathbf{sr})$ as the filter, modified by the scattering functions $g(s)$.

For a classical ergodic system on the energy surface $E = H(p,r)$, where the Hamiltonian, $H(p,r)$, has the standard form

$$H(p,r) = p^2/2m + V(r) \qquad (5)$$

Voros[31,32] has employed a semiclassical approximation by which the average Wigner function over the accessible chaotic part of phase space can be derived:

$$W(p,r) = \delta(E-H(p,r))/\int dr \int dp\ \delta(E-H(p,r)) \qquad (6)$$

where δ is Dirac's delta function. Performing the integration in eq 4 and taking eq 6 into account will yield, for randomly oriented molecules, diffraction intensities, $M(s)$, in the following form:

$$M(s) = (I_0/R^2)g(s)\{\int dr\ [(E - V(r))^{N/2-1}\Theta(E-V(r))] \times$$
$$(\sin(sr)/sr)/\int dr\ [(E - V(r))^{N/2-1}\Theta(E-V(r))]\} \qquad (7)$$

where $\Theta(E-V(r)) = 0$ for $E < V(r)$, $\Theta(E-V(r)) = 1$ for $E \geq V(r)$, and N is the number of degrees of freedom. Thus, all points on the surface of constant energy E are equally probable. As pointed out by Berry,[33] it is an important feature of the probability density function of chaotic motion, employed in eq 7, that it vanishes at the classical turning points and is zero outside of the classically accessible area $\Gamma(E)$, in contrast with the probability density functions describing regular motion.

In a time-independent Hamiltonian system, chaos can occur only if $N \geq 2$. For polyatomic molecular systems of bonded atoms it is suggested that, in the chaotic region, each internuclear distance is a three-dimensional random vector, with one degree of freedom removed due to bonding. In this case eq 7 simplifies to

$$M(s) = (I_0/R^2)g(s)\{\int_{\Gamma(E)}(\sin(sr)/sr)\, dr\} \qquad (8)$$

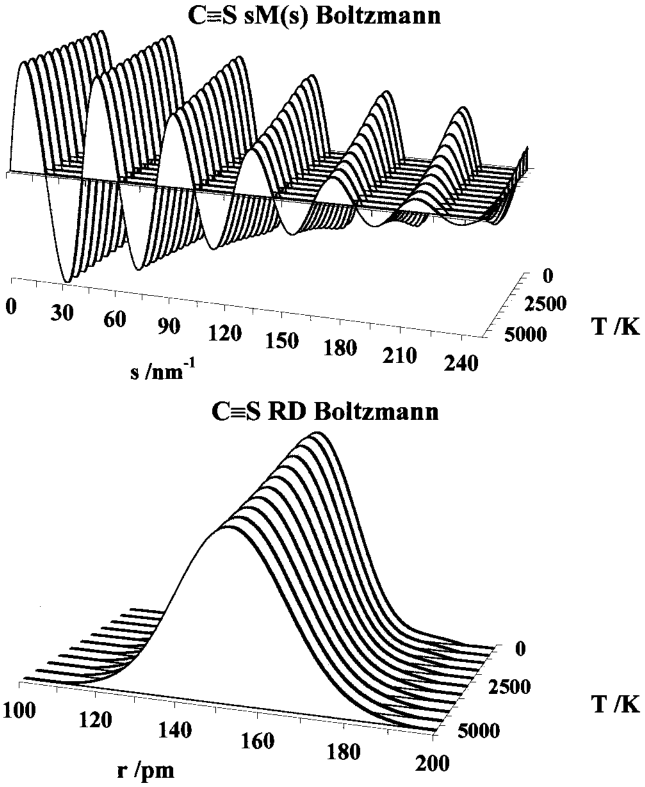

Figure 1. Theoretical electron diffraction intensities (upper) and radial distribution (RD) curves (lower) for carbon monosulfide (CS) in an equilibrium Boltzmann distribution over the temperature range from 0 to 5000 K. It is seen that the intensities exhibit an ever-increasing monotonic damping with increasing temperatures, in accord with traditional molecular scattering models. In the RD curves, essentially the Fourier transforms of the intensities, the same trend manifests itself through ever-broadening, Gaussian-like, peaks as the temperature increases.

The integration in eq 8 is over $\Gamma(E)$, where $E \geqslant V(r)$. In the polyatomic case, $V(r)$ is an internuclear pair potential; eq 8 has to be executed for each atom pair, and the total molecular intensities are the sum of the contributions of all the internuclear pairwise distances of the molecule.

Equation 8 is in agreement with the fact that all points on the surface of constant energy are equally probable, and consequently, the probability density in position space is uniform, which is the defining property of chaotic systems. Uniformity of the position space probability density for multidimensional chaotic systems is also predicted by the Akulin–Dykhne model,[34] which describes the excitation of a system with an irregular spectrum. This model was introduced for molecular excitation in a monochromatic laser field, and it predicts the existence of a zone of energy levels[34] in the vicinity of E_c. Uniformity of the spatial probability density function in the case of strongly chaotic systems is also suggested by the consideration that chaotic orbits in a conservative system tend to uniformly[35] visit all parts of a subspace of phase space.

Results and Discussion

To illustrate some aspects of the theory described above, we first considered the case of a one-dimensional harmonic oscillator. In real systems, chaotic nuclear motion can be established only in molecules with more than two atoms. However, since electron diffraction intensities depend mainly on pairwise internuclear distances, a diatomic molecule in a hypothetical chaotic state can serve as a good example to illustrate the manifestation of chaotic motion in electron diffraction data.

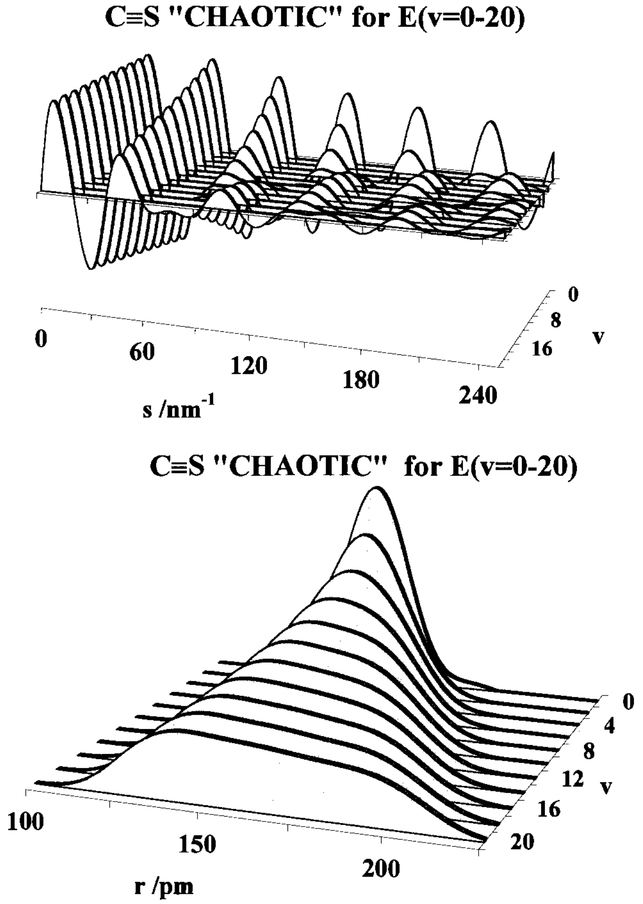

Figure 2. Theoretical electron diffraction intensities (upper) and RD curves (lower) for CS in a hypothetical “chaotic” distribution. The curves were modeled for arbitrary available energies of the chaotic system, which correspond to the first 20 vibrational levels of the nonchaotic molecule. In contrast to the equilibrium distributions (Figure 1), the intensities do not decline monotonically but instead exhibit an increasingly apparent phase reversal at higher scattering angles. The RD curves show an increasing breadth and flatness, corresponding to the spread in the turning points of the potential surface, and the uniform probability density of the model.

Connecting with previous studies,[7,8] we have selected carbon monosulfide as a test case. First, intensities and radial distribution (RD) curves were calculated for CS in an equilibrium Boltzmann vibrational distribution. As described previously,[7,8] these calculations were performed with variational wave functions[37] obtained by solving Schrödinger’s equation with an established potential function[36] of CS. The results are shown in Figure 1. Subsequently, corresponding intensities and RD curves, but for chaotic nuclear motion, were calculated using eq 8, for a series of arbitrarily selected energies (see Figure 2) which were used to calculate $\Gamma(E)$. Comparisons of Figures 1 and 2 show that the diffraction data and RD curves for CS are significantly different in the two states. In addition, it was found that the characteristic features of radial distribution associated with chaotic motion cannot be simulated by adjusting the level of vibrational energy in the procedures applying to regular motion.

As a second test case sulfur hexafluoride, SF_6, was selected because it is an effective model for illustrating the procedures described above and experimental electron diffraction data are available[38] in the temperature range up to 773 K, i.e., above the onset[39] of the quasi-continuum (QC) at 650 K.

Internuclear pair potentials of SF_6, obtained as described in ref 8, are shown in Figure 3. Diffraction intensities and RD curves for regular and chaotic motion are shown in Figures 4 and 5, respectively. As in the case of CS, it is seen that the characteristics of both the intensity and RD curves are significantly different for the two states. When the parameters of the regular state were refined to model any of the curves corresponding to the chaotic state, unrealistic results were obtained. These results are not unexpected because, in principle, it seems impossible to simulate the features of regular distributions by probability density functions which, like those applying to chaotic motion,[31−33] vanish at the classical turning points.

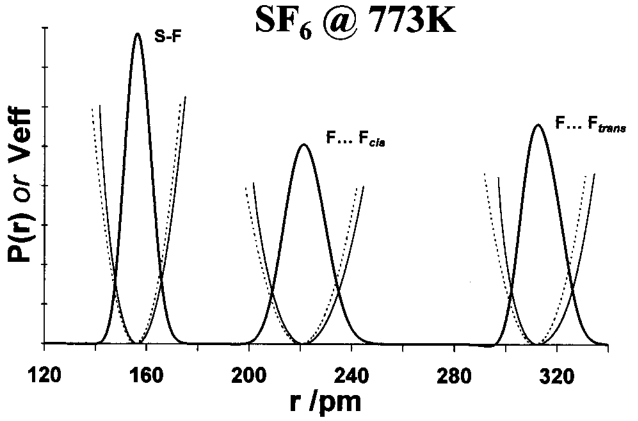

Figure 3. Experimental probability densities $P(r)$ and pairwise potentials $V(r)$ for the three internuclear distances of sulfur hexafluoride (SF_6) at an equilibrium temperature of 773 K. The $P(r)$ were derived from the stochastic modeling procedure of ref 8; the effective potentials shown are for the anharmonic (solid line) case, as derived from the data, and the harmonic case (dotted line), for comparison.

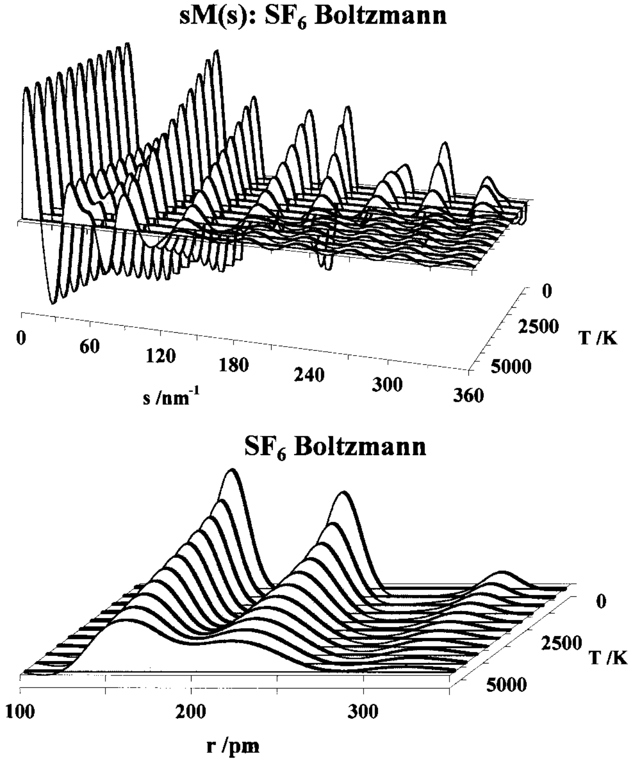

Figure 4. Theoretical electron diffraction intensities (upper) and radial distribution (RD) curves (lower) for SF_6 in an equilibrium Boltzmann distribution over the temperature range from 0 to 5000 K. Overall features are similar to those described in Figure 1, but with added beat patterns due to additional interference among the three internuclear distances present.

A previous electron diffraction study[38] of SF_6 has shown that, in equilibrium molecular ensembles at different temperatures

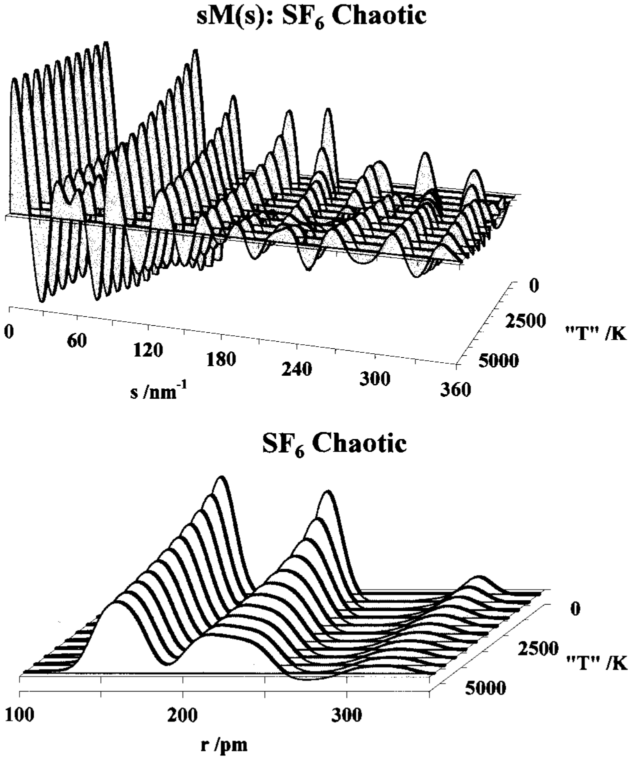

Figure 5. Theoretical electron diffraction intensities (upper) and radial distribution (RD) curves (lower) for SF$_6$ in a hypothetical chaotic state over a range of available energies corresponding to the temperatures shown; the foremost curves (5000 K) correspond to ~600 kJ mol^{-1}, distributed equally among the vibrational modes of the molecule. Classical turning points were derived from the experimental pairwise potentials shown in Figure 3. Other features of the curves are similar to those described in Figure 2.

between 293 and 773 K, the observed nuclear dynamics of this molecule are entirely consistent with the assumption of regular motion on an adiabatic potential energy surface in normal vibrational coordinates. Apart from the general features of the data, this conclusion is strongly suggested by the fact that the equilibrium internuclear distance, r_e(S−F), is independent of temperature in the whole temperature range within ±0.08 pm.[38] This result is interesting because Bloembergen et al.[39] have found that, in collisionless multiphoton absorption studies of SF$_6$ with picosecond CO$_2$ laser pulses, the vibrational temperature of 650 K is hot enough for SF$_6$ to be considered in the QC,[29,39] which is characterized[27−29] by a high density of states, i.e., $\rho(E) > 10$ per cm^{-1}.

Conclusions

The material presented above shows that, in principle, electron diffraction data can provide clear signatures of the onset of chaotic nuclear dynamics, in contrast to regular nuclear motion, in polyatomic molecules.

For the specific case of SF$_6$ our results indicate that, above the appearance of the QC at 650 K[39] and up to 773 K, the nuclear dynamics of the molecule do not exhibit the characteristic features of chaotic nuclear motion. This result is noteworthy because complications of optical spectra, which are observed concomitantly with the appearance of the QC, are often rationalized as manifestations of the onset of chaotic nuclear dynamics.

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