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Hyper-Rayleigh spectral intensities of gaseous Kr–Xe mixture

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Binary collision-induced hyper-Rayleigh (CIHR) spectra of Kr–Xe gaseous system are computed quantum mechanically and classically within the frequency range up to 380 cm\(^{-1}\). The intensities are expressed in absolute units. The details of the theory developed for the CIHR spectra are given and the properties of the profiles as well as the depolarization ratio frequency dependence are discussed. The contributions to the spectra related to the vector \(\vec{b}_{10}(r)\) and the septon \(\vec{b}_{30}(r)\) components of the hyperpolarizability tensor are evaluated. © 2005 American Institute of Physics. [DOI: 10.1063/1.1925267]

I. INTRODUCTION

Among the numerous nonlinear optics phenomena caused by light of high intensity, scattering is one of the most widely studied despite the difficulty that besets its observation. This is a result of the fact that the light scattering is an elementary process whereby the reaction of the medium to the incident light wave is apparent in the simplest way. The possibility of the nonlinear scattering of light had been considered long before the coming of lasers. In the phenomena of this kind the nonlinear response of the medium to the incident light beam leads to the emergence of scattered higher harmonic component in addition to the linear component at \(\omega_l\), the incident laser frequency. These processes are referred to as multiharmonic scattering (MS). One of the best known among the MS effects and widely studied currently, both theoretically and experimentally, is the hyper-Rayleigh (HR) scattering which is a three-photon event in which a system is excited with two photons of the laser frequency \(\omega_l\) and spontaneously emits one photon at a frequency of about \(2\omega_l\).\textsuperscript{1,2} Kičič\textsuperscript{3,4} proposed a compact and deep-reaching theory of multipolar harmonic scattering within both classical and quantum treatments (see also Refs. 5–8).

According to the theory, at the double frequency \(2\omega_l\), the main quantity responsible for the nonlinear response of the system is the first hyperpolarizability tensor \(\mathbf{b}\). This is a third rank tensor, odd under coordinate inversion, whereas the inversion leaves a centrosymmetric molecule and, consequently the \(\mathbf{b}\) tensor. Hence, \(\mathbf{b}\) must vanish identically for centrosymmetric systems. Nevertheless, the light scattered at frequencies around \(2\omega_l\) in systems composed of centrosymmetric molecules has been observed; this effect being attributed to the so-called collision-induced (CI) components of the \(\mathbf{b}\) tensor which result from the interactions between the constituent molecules of the scattering media.

A pair of atoms of the same type exhibits a center of symmetry, so the collision-induced pair hyperpolarizability can be expected only for mixtures of unlike atoms.\textsuperscript{8–12} Recently, several studies have been performed\textsuperscript{13–17} reporting the hyperpolarizability computations for heterodiatomic supermolecules. In our previous work\textsuperscript{12} we considered the HR spectrum of Ne-Ar mixture. In this paper, we present a theory and numerical calculations of the hyper-Rayleigh spectrum of Kr–Xe mixture. The details of the theory of the CIHR spectrum have been given and computations have been performed in absolute units. As far as we are aware, this is the first result of this kind. In the numerical calculations of the profiles, the CI hyperpolarizabilities obtained on the basis of quantum-chemistry methods have been applied.\textsuperscript{16} The frequency-dependent depolarization ratio \(D^{2\omega_l}(\nu)\) of the hyper-Rayleigh scattered light is also computed.

II. THEORETICAL CONSIDERATIONS

A pair of unlike atoms forms a short-time (of order \(10^{-13}\) s) noncentrosymmetric supermolecule of the \(C_{nu}\) symmetry. Its leading nonlinear optical properties are given by the collision-induced hyperpolarizability tensor \(\mathbf{b}\). Hence, the hyper-Rayleigh spectrum of such a system is due to the diatom collision (interaction)-induced hyperpolarizability and quantum and/or classical dynamics of the diatom.

The wave functions of the relative motion of the two atoms of the supermolecule separated by the distance \(\mathbf{r}\) are given by\textsuperscript{18,19}

\[ |i\rangle = |nlm\rangle = Y_{lm}(\hat{\mathbf{r}}) \frac{R_i(\mathbf{r})}{r}, \]

where the angular part of the product is given by the spherical harmonic \(Y_{lm}(\hat{\mathbf{r}})\), whereas \(R_i(\mathbf{r})\) is the radial wave function for state \(i\).

In order to develop quantities describing spectral properties of the HR scattered light we extend the Gordon\textsuperscript{20} formula for the linear scattering double differential cross section (DDCS) to the hyper-Rayleigh scattering case. However, for
nonlinear processes, it is not easy to determine it. Therefore, for the hyper-Rayleigh scattering we have decided to define and calculate a double differential intensity per supermolecule (diatom) scattered into a frequency \(d\omega\) with a solid angle \(d\Omega\) and normalized to the square of the intensity of the incident radiation \(I_0\) (which will be from here on denoted as NDDI—normalized double differential intensity). To begin with, we consider a general scattering geometry when the incident radiation is polarized in the arbitrary direction \(e\) and the scattered light is measured behind an analyzer of arbitrary polarization \(n\). Then, for the quantum transition \(i \rightarrow i'\) we obtain
\[
\frac{\partial^2 I_{\omega i i'}}{\partial \Omega \partial \omega}_{\text{HR}} = \frac{\pi}{2c} k^4 \sum_{i,i'} \rho_i (i' | n \cdot \mathbf{e} | i) |^2 \delta(\omega - \omega_{i'i}),
\]
where \(\hbar \omega_{i'i'} = E_{i'} - E_i\), \(\rho_i\) is the density-matrix element of the initial state \(i\), and \(k_i\) stands for the wave vector of the scattered light.

Now, we simplify our light scattering geometry to the usually used right angle case. We assume the incident light propagating along the \(Y\) axis with the electric vector vibrating along the \(Z\) axis. The scattered light is observed along the \(X\) direction axis. As a consequence, the total scattered intensity can be divided into two components: a vertical depolarized component. According to Eq. (A1), we notice that \(b_{zzz}\) and \(b_{xxz}=b_{xz}=b_{zzz}\) are independent, namely, \(\vec{b}_{zzz}=\vec{b}_{xxz}=\vec{b}_{zzz}\). It simplifies the spherical representation of the \(b\) tensor to the form:

\[
\bar{b}^{000}_{111} = \bar{b}_{zzz},
\]
\[
\bar{b}^{011}_{111} = \bar{b}^{011}_{111} = \bar{b}^{110}_{111} = \bar{b}^{110}_{111} = -\bar{b}_{xxz}.
\]

The irreducible polarizability tensors are constructed from the standard coupling methods:

\[
\bar{b}_{1l} = \sum_{m_1,m_2} C^{m_1}_{m_1,m_2} c_{m_1,m_2}^{00} c_{m_1+m_2,11}^{11} \times \bar{b}^{m_1+m_2}_{01},
\]

where \(C^{m_1}_{m_1,m_2}\) stands for the Clebsch–Gordan coefficient. For \(l=3\) the \(a\) parameter must be equal 2; whereas for \(l=1\) we also have \(a=0\) and \(a=1\). For \(a=1\) the sum in Eq. (A7) vanishes. To get the totally symmetric part of the \(b\) tensor, the following transformation using genealogical coefficients is necessary:

\[
\bar{b}_{10} = \frac{1}{3} \{ \sqrt{5} \bar{b}_{10}[(11)01] + 2 \bar{b}_{10}[(11)21] \}.
\]

Consequently, for the irreducible spherical tensor components of \(\vec{b}\) we obtain

\[
\bar{b}_{10} = -\sqrt{\frac{5}{3}} (\bar{b}_{zzz} + 2 \bar{b}_{xxz}),
\]
\[
\bar{b}_{30} = \sqrt{\frac{2}{3}} (\bar{b}_{zzz} - 3 \bar{b}_{xxz}).
\]

In the theoretical considerations presented here we use the spherical irreducible \(\bar{b}_{10}\) and \(\bar{b}_{30}\) components of the hyperpolarizability tensor since they appear in a natural way, as, e.g., in Eq. (A4). In some instances, however, other expressions are more convenient. In our previous work as well as in the numerical section below we refer rather to the tensorial invariants \(b_1\) and \(b_3\) closely related both to the notation \(b_1 = \bar{b}\) and \(b_3 = \Delta \beta\) used by Buckingham and Maroulis and Haskopoulos and to the above-mentioned quantities:
\[ \vec{b}_{10} = -\sqrt{2/3} \vec{b} - \sqrt{1/3} \vec{b}_1, \]
\[ \vec{b}_{30} = \sqrt{2/3} \Delta \vec{b} = \sqrt{1/3} \vec{b}_3. \]

On applying transformation rules for the spherical tensors in Eqs. (5) together with the Wigner–Eckart theorem and appropriate orthogonality conditions for the \(3-j\) Wigner coefficients, the angular part can be expressed via the terms of the shape:

\[ \sum_{mm'} \langle l'm' | \text{coeff} \sqrt{\frac{4\pi}{2l+1}} Y_{km}(\hat{r}) | lm \rangle^2 = |\text{coeff}|^2 \frac{2l+1}{2k+1} H(k)_{l'}, \]

where the numerical factors \(\text{coeff}\) stem from the spherical-Cartesian tensor transformation in Eq. (5), while for the \(H(k)_{l'}\) we obtain

\[ H(k)_{l'} = (2l' + 1) \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2, \]

the coefficients that can be directly compared to the \(b_{1l}\) ones introduced by Placzek and Teller\(^{27}\) for the linear scattering \((k=2)\).

By Eqs. (3), (5), (11), and (12) the appropriate expression for the NDDI of the hyper-Rayleigh spectra for the polarized component reads

\[ \left( \frac{\partial^2 I_{ZZ}}{\partial \Omega \partial \omega} \right) / I_0^2 = \frac{\pi}{2c} k^4 \sum_{i,l} \rho_i \left\{ (2l+1) \left[ \frac{1}{2} H(1)_{l'} |(\vec{b}_{10})_{l'}|^2 \right. \\
+ \frac{3}{5} H(3)_{l'} |(\vec{b}_{30})_{l'}|^2 \right] \delta(\omega - \omega_{1l'}) \right\}, \]

whereas for the depolarized component we obtain

\[ \left( \frac{\partial^2 I_{YZ}}{\partial \Omega \partial \omega} \right) / I_0^2 = \frac{\pi}{2c} k^4 \sum_{i,l} \rho_i \left\{ (2l+1) \left[ \frac{1}{2} H(1)_{l'} |(\vec{b}_{10})_{l'}|^2 \right. \\
+ \frac{1}{10} H(3)_{l'} |(\vec{b}_{30})_{l'}|^2 \right] \delta(\omega - \omega_{1l'}) \right\}, \]

where

\[ (\vec{b}_{10})_{l'} = \int_0^\infty R_{l'z}(r) \vec{b}_{10}(r) R_z(r) dr \]

is the radial matrix element of the \(\vec{b}_{10}(r)\) component of the collision-induced hyperpolarizability tensor. \(R_z(r)\) is the radial wave function with energy \(E\) and the angular momentum quantum number \(l\), whereas for \(R_{l'z}(r)\) the wave function corresponds, respectively, to \(E'\) and \(l'\).

When unpolarized detectors are used, the scattered intensity is a sum of two signals with orthogonal polarizations. Then the numerical coefficients in formulas defining the intensity for unpolarized detectors [analogical to Eqs. (14) and (15)] read, respectively, \(\frac{\pi}{2c}\) and \(\frac{\pi}{21}\) for the polarized component \(I_1\) (the incident light polarization perpendicular to the scattering plane), while for the depolarized component \(I_2\) (the incident light polarization parallel to the scattering plane) they are equal; \(\frac{\pi}{21}\) and \(\frac{\pi}{21}\). From Eqs. (14) and (15) we notice that in the hyper–Rayleigh case there are a dipolar/vector type \((k=1)\) and an octopolar/septor type \((k=3)\) contributions to the scattered intensity. For the dipole type components of \(b\) we have

\[ H(1)_{l'1} = \frac{l+1}{2l+1}, \quad \Delta l = +1, \]

\[ H(1)_{l'3} = \frac{l}{2l+1}, \quad \Delta l = -1, \]

which are identical with those calculated in the infrared absorption theory.\(^{19}\) For the octopolar type components of \(b\) we obtain

\[ H(3)_{l'1} = \frac{3}{2} \frac{l(l+1)(l+2)}{2(2l+5)(2l-1)(2l+1)}, \quad \Delta l = +1, \]

\[ H(3)_{l'3} = \frac{3}{2} \frac{l(l-1)(l+1)}{2(2l+3)(2l-3)(2l+1)}, \quad \Delta l = -1, \]

\[ H(3)_{l'5} = \frac{5}{2} \frac{l(l+1)(l+2)(l+3)}{2(2l+1)(2l+3)(2l+5)}, \quad \Delta l = +3, \]

\[ H(3)_{l'3} = \frac{5}{2} \frac{l(l-1)(l-2)}{2(2l+1)(2l-1)(2l-3)}, \quad \Delta l = -3. \]

### B. Radial part

The basic quantity to be counted when dealing with the radial part of NDDI is the matrix element of the radial-dependent component of the hyperpolarizability tensor:

\[ B_{k0}(\omega) = \sum_{i,l} (2l+1) H(k)_{li} e^{-\mu E_i} Z \times \int_0^\infty |R_{E_i}(r) \vec{b}_{k0}(r) R_{E_i}(r) dr|^2 \delta(\omega - \omega_{Ei}). \]

Following the usual path of calculation of such integrals, we arrive at

\[ B_{k0}(\omega) = \frac{L_0^3}{V} \frac{2\mu}{\hbar \pi^2} \sum_{l,\Delta l} (2l+1) H(k)_{li} \times \int_0^\infty dE (EE')^{\frac{3}{2}} e^{-\mu E} |(\vec{b}_{k0})_{li}(E,\omega)|^2, \]

where

\[ |(\vec{b}_{k0})_{li}(E,\omega)|^2 = \left| \int_0^\infty \vec{R}'(r;E',l') \vec{b}_{k0}(r) \hat{R}(r;E,l) dr \right|^2, \]

\[ E' = E + \hbar \omega \]
and $\mu$ is the reduced mass of the supermolecule, $L_0$ is the thermal De Broglie wavelength of the relative motion of two atoms and $V$ is the active scattering volume. After changing the normalization conditions, Eq. (21) finally leads to

$$B_{k0}(\omega) = \frac{L_0^3}{V} \sum_{l,i,l'} (2l + 1)H(k)^{ij}_l(\bar{B}_{k0})^{ij}_l(\omega), \quad (23)$$

where

$$\bar{B}_{k0}^{ij}_l(\omega) = \int_0^\infty dEe^{-\beta E}|(\tilde{b}_{k0})^{ij}_l(E,\omega)|^2. \quad (24)$$

Thus, according to Eqs. (14) and (23), for the polarized component of the the hyper-Rayleigh scattering the following relation holds:

$$\mathcal{J}_{zz}^{\text{per unit volume}}(\nu) = \int_0^\infty \mathcal{J}_{zz}^{\text{per unit volume}}(\nu). \quad (26)$$

Then, for the spectral distribution of the polarized component of the HR scattered light per unit volume irradiated, we obtain

$$\left[ \frac{\partial \mathcal{J}_{zz}^{\text{per unit volume}}}{\partial \Omega \partial \nu} \right] / I_0 = \mathcal{J}_{zz}^{\text{per unit volume}}(\nu). \quad (27)$$

where $n_i$ denotes the partial number density of a component $i$ and similarly for the depolarized component.

We note that for $\mathcal{J}_{zz}^{\text{per unit volume}}(\nu)$, according to Eq. (25) and having in mind that $[b]=[\text{cm}^3 \text{erg}^{-1}]^{1/2}$, we obtain $[\mathcal{J}_{zz}^{\text{per unit volume}}(\nu)] = \text{cm}^8 \text{s}^{-1}$. Taking into account that $[I_0]=\text{erg cm}^{-2} \text{s}^{-1}$, the double differential intensity of HR scattering is of the dimension $[(\partial \mathcal{J}_{zz}^{\text{per unit volume}})/\partial \Omega \partial \nu] = \text{erg cm}^{-1}$. We shall use these relations in the numerical calculations presented in the following part of our work.

III. NUMERICAL CONSIDERATIONS

The quantum-mechanical theoretical approach outlined in Sec. II forms a firm basis for a convenient routine of numerical calculations of the hyper-Rayleigh spectra. The matrix elements in Eq. (22) can be evaluated towards resulting spectral profiles provided that an appropriate quantum-mechanical numerical method of solving the Schrödinger equation for the molecular system of interest is at hand. A number of such procedures have been developed, one of them successfully applied by the authors of this work for the hyper-Rayleigh Ne–Ar spectra in Ref. 12. It must be recalled here that the pairs of Kr and Xe, due to their relatively large masses, may be regarded as more classical and, consequently, they usually require long and time consuming calculations including a numerous set of the partial waves for a large range of the angular momentum $l$ quantum numbers. Therefore, if appropriate accuracy of the final results is to be achieved with a reasonable computer workload applied, one has to apply an efficient algorithm and a code including substantially CPU time saving procedures. The so-called complex-plane method of solving differential equations and calculating necessary matrix elements has been proved to meet the requirement.28 Another possible approach for the numerical evaluation of spectral profiles for systems consisting of relatively heavy components might be to treat the problem in the entirely classical manner. In this work we concentrate on developing a general quantum theory suitable also when considering systems of light atomic pairs (which we take into account in our following work being currently in progress). Nevertheless, for comparison and benchmarking purposes, we shall present in the section below the profiles obtained by means of the classical approach.

In order to perform the numerical calculations of the spectral profiles, there are two raw datasets needed in addition to the above computing procedure. First, it is inevitable to have a functional form of the hyperpolarizability tensor dependence on the interatomic distance and secondly, a reliable potential curves describing interactions between constituent atoms of a supermolecule.

A. Collisional hyperpolarizabilities

A number of analytical and numerical methods of evaluating collisional properties have been developed. Treated as a first approach effect, the multipolar approximation diatomic tensorial invariants, though expressed in a convenient analytical form, are generally valid for systems consisting of rather complex molecules interacting at relatively long inter-
molecular separations. Therefore, for the case considered in this work, with the noble gas diatoms involved, we have decided to develop the collisional spectral profiles using the pair hyperpolarizability values obtained by having recourse to the so-called \textit{ab initio} procedures of quantum chemistry. Fortunately, a vast number of such methods have been developed and applied in recent years.\cite{14,15,17} Of those, the datasets obtained by Maroulis and Haskopoulos\cite{14,15} provide exceptionally wide range of \( r \) distances including very small interatomic separations. In the previous work of the series\cite{12} we successfully applied their datasets for Ne–Ar systems. Here we also use the results produced by the Maroulis’ group for Kr–Xe pairs.\cite{16} They have been computed by means of the second-order Møller–Plesset perturbation theory (MP2) with the [8s7p6d5f1/9s8p7d5f] basis set. These data are discrete sets of values and should be fitted to a functional analytical dependence, so that they could be used in our computing methods. It can be easily done by means of a method analogical to the one used in Ref. 12. Likewise, we apply here fitting functions of relatively simple form of a sum of some exponential terms and inverse powers of the interatomic distance. The fitting procedure used is the well-known nonlinear least-squares Marquardt–Levenberg\cite{29} (the reader should refer to Ref. 12 for the details of the calculations; functional formulas and fitted parameters for Kr–Xe can be obtained on demand form glaz@amu.edu.pl). The dipolar \( b_1(r) \) and octopolar \( b_6(r) \) components of the hyperpolarizability tensor are shown in Figs. 1(a) and 1(b), respectively. One can easily notice that the fitted profiles are in a quite good agreement with the dataset points. The root-mean-square deviation (RMSD) between the dataset points and the fitted curve is of order of \( \sim 0.01 \) for \( b_1 \) and \( \sim 0.03 \) for \( b_6 \), compared with \( \sim 0.02 \) and \( \sim 0.06 \), respectively, for the RMSD due to the roundoff error of the original \textit{ab initio} calculations.

Mentioning some specific properties of \( b(r) \) may be noteworthy here. First, let us notice that the \( b_1(r) \) profile shows a profound negative well for short interatomic separations, whereas in the case of the previously studied system of Ne–Ar all of the functions but one (B3LYP model) are exclusively positive.\cite{12} On the other hand, the \( b_6(r) \) component—unlike in the Ne–Ar case—does not reach negative values. Instead, it goes through a characteristic pattern of minimum/maximum shape within the short distance range. As we shall see, this kind of behavior of the \( b(r) \) functions reflects in some of the features of resulting spectral profiles. The multipole contribution to \( b_6(r) \) has been included in the fitting expressions, yet seemingly it does not play a significant role but for relatively long intermolecular separations.

B. Potential

As far as the interaction potential is concerned, in our previous work\cite{12} we apply—treated as a first approach approximation—the well-known, yet rather crude, Lennard-Jones 12-6 function. In this work, however, we shall refer to a more sophisticated model. Seemingly, there is a rather limited number of appropriate potential surfaces for Kr–Xe proposed in literature,\cite{30} the most suitable for our purposes being the concept developed by Pack et al.\cite{30} This potential is given in terms of analytical expressions and is based on the so-called Morse-spline-van der Waals model (M3SV). All the formulas and parameters used by us are listed in Ref. 30. The shape of the potential is shown in Fig. 2.

C. Calculations

1. Quantum spectrum

Much of the details of the quantum calculations is outlined in Refs. 12, 28, and 32 and in the articles cited there. Customarily based on the Numerov method of solving differential equations adapted to computations performed in the complex plane, the procedure can cope successfully with the

![FIG. 1. (a) The dipolar \( b_1(r) \) hyperpolarizability component vs the interatomic distance. (b) The octopolar \( b_6(r) \) hyperpolarizability component vs the interatomic distance (Ref. 16).](Image)

![FIG. 2. The interaction potential for KrXe diatom after Ref. 30.](Image)
numerical propagation/cancellation errors, especially notorious when high-frequency spectral profiles are to be treated. Although, in general, the routine provides reasonable CPU time savings, for systems such as Kr–Xe even this approach suffers from lengthy and numerous computing steps, necessary so that desired convergence and acceptable accuracy might be achieved. Owing to the classical behavior of the supermolecule considered, the range of the quantum \( l \) numbers and, consequently, the set of the partial functions that should be taken into account, are relatively large when compared with lighter diatoms. As a result, we have found that the uppermost value of \( l \) should reach as far as 350.

The characteristics of the other parameters involved are mainly determined by features such as the potential and the hyperpolarizability dependence on the interatomic distance, \( r \). According to safe estimation, desirable convergence of the calculations can be gained with \( r \) ranging from the region closely approaching the steep repulsive wall of the potential to the distances of negligible potential strength. A thorough analysis based on these criteria leads to \( r_{\text{min}} \approx 0.77 \text{\AA} \) and \( r_{\text{max}} = 10.0 \text{\AA} \) with up to 10,000 grid points in between.

Finally, initial energies of the colliding atoms rendering convergent matrix elements cover values from 0.02\( e \) up to 540\( e \) \((e=7.33 \times 10^{-4} \text{\,h \,a.u.})\).

In our calculations only the energies related to free pair transitions were taken into account. Obviously though, the bond and quasibond states are also possible. Yet, as it is known from other studies, they are apparently important mainly for the frequencies close to the central part of the profile around \( v=0 \), and therefore they do not affect the overall wide remaining part of the spectrum. Moreover, these contributions can be calculated and added by well-known methods when necessary.

On applying the above-mentioned parameter values in the quantum computing routine, we arrive at the collisional spectral profiles shown in Figs. 3 and 4, of which the former figure illustrates a comparison between the classical and quantum features. The results will be discussed in more a detailed manner in the last section of the study.

2. Classical spectrum

A standard procedure \(^{18,33,34}\) has been used to compute the classical trajectories of colliding atoms characterized by the polar coordinates \([r(t), \theta(t)]\) at a time \( t \) for a given Kr–Xe intermolecular potential \( U(r) \) and every possible value of \( b \), the impact parameter and \( s \), the relative velocity of the encounter. Taking into account these free dimer trajectories, the Fourier transforms of the vector \( b_{10}(r) \) and the separt \( b_{30}(r) \) components of the hyperpolarizability tensor can be computed according to the Posch formulas \(^{33}\):

\[
B_{3}(v,b,s) = \frac{1}{2} \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \cos(2\pi v t) \cos[3 \theta(t,b,s)] dt \right]^{2} + 3 \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \cos(2\pi v t) \cos[\theta(t,b,s)] dt \right]^{2} + 5 \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \sin(2\pi v t) \sin[3 \theta(t,b,s)] dt \right]^{2},
\]

\[(28)\]

FIG. 3. Comparison of the polarized quantum-mechanical and classical hyper-Rayleigh light scattering spectrum for Kr–Xe pairs at \( T=295 \text{\,K} \). The separt part of the HR spectrum is displayed here.

\[
B_{3}(v,b,s) = \frac{1}{2} \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \cos(2\pi v t) \cos[3 \theta(t,b,s)] dt \right]^{2} + 3 \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \cos(2\pi v t) \cos[\theta(t,b,s)] dt \right]^{2} + 5 \left[ \int_{0}^{\infty} b_{30}[r(t,b,s)] \sin(2\pi v t) \sin[3 \theta(t,b,s)] dt \right]^{2},
\]

\[(28)\]

FIG. 4. The quantum-mechanical-polarized hyper-Rayleigh \( J_{\text{pol}}^{\text{2H}}(v) \) light scattering spectrum for Kr–Xe pairs at \( T=295 \text{\,K} \) (quantum-mechanical results). The normalized double differential intensity is given in the absolute units (see the text).
We found that $V(b_2^2)$ is the scattering volume $M_k$ in the above data to the free dimer integrals $x_i$. The integrals $M_k$ and $V(b_2^2)$ are expressed in cm$^2$ erg$^{-1}$. The ratios $x_i$ giving momentum portions due to free dimers are dimensionless.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$V(b_2^2)$</th>
<th>$x_i$</th>
<th>$x_iV(b_2^2)$</th>
<th>$M_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$3.283 \times 10^{-84}$</td>
<td>0.748</td>
<td>$2.455 \times 10^{-84}$</td>
<td>$2.454 \times 10^{-84}$</td>
</tr>
<tr>
<td>3</td>
<td>$5.534 \times 10^{-84}$</td>
<td>0.768</td>
<td>$4.251 \times 10^{-84}$</td>
<td>$4.226 \times 10^{-84}$</td>
</tr>
</tbody>
</table>

The corresponding spectral absolute intensities scattered by a scattering volume $V$ may be derived analogically to those given for the linear scattering: \[ I_1(\nu) = \frac{\pi}{2e} k_0^2 g(\nu)c \int_0^\infty s f_{MB}(s,T)4\pi s^2 ds \times \int_0^\infty B_1(v,b,s)2\pi dbd, \] \[ I_3(\nu) = \frac{\pi}{2e} k_0^2 g(\nu)c \int_0^\infty s f_{MB}(s,T)4\pi s^2 ds \times \int_0^\infty B_3(v,b,s)2\pi dbd, \]

where $f_{MB}(s,T)4\pi s^2 ds$ stands for the Maxwell–Boltzmann factor, $k_0$ is the wave vector of the scattered light at $k_0/2$, and $g(\nu)=\exp(h\nu/(2k_0T))$ is the detailed balance correction. It is worth noting that using a similar procedure for argon, we found the isotropic and anisotropic Rayleigh spectra in absolute units very close to those obtained by quantum mechanics.\(^3\) For the vector ($k=1$) and septr ($k=3$) components of the hyperpolarizability tensor we compute the zeroth moment of the respective parts of the HR spectrum according to the sum rule procedure:

\[ V(b_2^2) = \int_0^\infty b_2(r)^2 \exp\left(-\frac{U(r)}{k_0T}\right) 4\pi r^2 dr. \]

To check our numerical results and procedures we compare the above data to the free dimer integrated intensities $M_k$ resulting for vector and septr components of the HR spectral distributions:

\[ M_k = \frac{4c}{\pi k_0^2} \int_0^\infty I_k(\nu)g(\nu)^{-1} d\nu. \]

We found that $M_k=x_iV(b_2^2)$, (where $x_i$ is the proportion of the momenta due to free dimers\(^3\)) which may be checked in Table I. Finally, for the polarized $J_{zz}^\nu(\nu)$ and the depolarized $J_{zz}^\nu(\nu)$ the hyper-Rayleigh spectra considered quantum mechanically in the preceding section we obtain:

\[ J_{zz}^\nu(\nu) = \frac{1}{2} I_1(\nu) + \frac{2}{15} I_3(\nu), \]

\[ J_{zz}^\nu(\nu) = \frac{1}{5} I_1(\nu) + \frac{1}{15} I_3(\nu). \]

These spectra are provided in Fig. 3 (just the septr contribution of $J_{zz}^\nu$) together with the corresponding quantum-mechanical calculations and in Fig. 5—the depolarized component.

**IV. RESULTS, DISCUSSION, AND CONCLUSION**

We computed the hyper-Rayleigh binary collision-induced spectra for gaseous Kr–Xe mixture at 295 K. To this end, we have developed a quantum theory of the CHR scattering, which provides a handy tool for numerical evaluation of quantum spectral profiles. In addition, a classical approach has been applied and the results of the two methods compared. They are shown in Fig. 3, where only the septr components of the total effect are illustrated as an example (the vector parts reveal similar properties). The figure presents remarkable agreement between the classical and quantum results: the two lines are barely separable except for several points around the very specific region close to $\nu \sim 200$ cm$^{-1}$ and then for the very far tail of the profile. It comes as no surprise, as—according to a numerical estimation—the root-mean-square deviation between the two spectral functions reaches no more than $\sim 0.025$ for the wide range of the low midfrequencies ($\nu \sim 150$ cm$^{-1}$), with points where the relative deviation does not exceed the value of 1%. For higher frequencies ($\nu \gg 180$ cm$^{-1}$) the picture is slightly less satisfactory, with RMSD $\sim 0.06$. This discrepancy can be supposedly attributed to physical and/or numerical factors. If the latter is the case, a more refined and restrictive treatment of the computing routine might bring forth even better agreement if necessary. Nevertheless, we do believe that the discussed comparison between the classical and quantum results can serve as a solid proof of validity of both—the quantum formulas obtained as well as the quantum-mechanical in the preceding section we obtain:

\[ J_{zz}^\nu(\nu) = \frac{1}{2} I_1(\nu) + \frac{2}{15} I_3(\nu), \]
The strong influence of the septor \( b_3 \) component is visible at low frequencies (about 0–30 cm\(^{-1}\)) and for the high-frequency values (about 220–300 cm\(^{-1}\)). The results of quantum (---) and classical (–) computations are shown.

Interestingly though, quite visibly the function exceeds this value, especially within the convex part of the graph. This is clearly visible in the low-frequency region in Fig. 5 and finally in the frequency dependence of the depolarization ratio.

To sum up, in this work the hyper-Rayleigh binary spectra for a Kr–Xe gaseous mixture are computed both quantum mechanically and classically. The frequency-dependent HR depolarization ratio \( D^{222}(v) \) is calculated as well. The purely collision-induced depolarized Kr–Xe Rayleigh light scattering spectrum is also obtained for the same conditions.

To the best of our knowledge, for the first time, the CIHR spectra are given in the absolute units, which—we do believe—should offer a helpful contribution to the field of the gaseous collision–induced experimental spectroscopy.
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