Vibrational coherence of I₂ in solid Kr

M. Karavitis and V. A. Apkarian

Department of Chemistry, University of California, Irvine, California 92697-2025

(Received 26 September 2003; accepted 9 October 2003)

Time-resolved coherent anti-Stokes Raman scattering, with a resolution of 20 fs, is used to prepare a broadband vibrational superposition on the ground electronic state of I₂ isolated in solid Kr. The coherent evolution of a packet consisting of ν=1–6 is monitored for as many as 1000 periods, allowing a precise analysis of the material response and radiation coherence. The molecular vibrations are characterized by ωₓ=211.330(2) cm⁻¹, ωᵧ=0.6523(6) cm⁻¹, ωz=2.9(1)×10⁻³ cm⁻¹; the dephasing rates at 32 K range from 110 ps for ν=1 to 34 ps for ν=6, with ν dependence: γ(ν)=8.5×10⁻³+4.9×10⁻⁴ν²+2.1×10⁻⁶ν⁴ ps⁻¹. The signal amplitude is also modulated at ωq=41.56(3) cm⁻¹; which can be interpreted as coupling between the molecule and a local mode. The surprising implication is that this resonant local mode is decoupled from the lattice phonons, a finding that cannot be rationalized based on a normal-mode analysis. © 2004 American Institute of Physics. [DOI: 10.1063/1.1630567]

INTRODUCTION

Molecular iodine isolated in rare-gas solids provides a prototype for the scrutiny of condensed phase dynamics. Since this model system is amenable to explicit, nearly exact analysis, detailed experimental data could be useful in the formulation and testing of reduced descriptions of vibrational dynamics in condensed matter. Prior to the recent time-resolved coherent anti-Stokes Raman scattering (TRCARS) measurements in solid Ar,¹ save for the resonant Raman spectra recorded with instrument limited resolution,²,³ there were no experimental data on the vibrational dynamics of matrix isolated I₂ in its ground electronic state. The related experiments on energy flow in high-lying vibrations of iodine in the liquid phase⁴ have played a central role in the construction and testing of models of vibrational relaxation in condensed media.⁵⁻⁷ The extent to which these results can be extrapolated to the lower states where vibrational levels become defined, or to the denser solid state, is not clear. Indeed, experimental studies of vibrational relaxation in rare-gas solids has been limited for the most part to infrared active molecules, such as NH/ND,⁸⁻¹⁰ OH/OD,¹¹ HCl,¹² NO,¹³ CO.¹⁴ In all these cases the vibrational frequencies are well removed from the phonon density of states, leading to long relaxation times that could be directly measured through infrared fluorescence, with typical detection response times of >10⁻⁸ s.¹⁵⁻¹⁷ With the availability of intense short pulse sources, this status is changing.¹⁸ Beside our four-wave mixing measurements, Broquier et al. have conducted infrared photon echo measurements of vibrational dynamics in such systems as DCI and CO.¹⁹,²⁰ The mechanical process of vibrational relaxation and dephasing of a homonuclear diatomic in the van der Waals solid of rare gases, with internal frequencies that are not far removed from the Debye limit, is an important case study. Given the sophistication with which I₂–Rg interactions have been scrutinized,²¹⁻²³ and have already been implemented in both dynamical²⁴,²⁵ and static²⁶ calculations of the molecule trapped in rare-gas solids, explicit treatments of dephasing and dissipation could be expected. Our intention is to provide the requisite experimental database for such scrutiny. The experiments in solid Ar were limited in this respect because of the unavoidable multiphonon induced dissociation of the molecule during TRCARS measurements.²⁷ As such, we resorted to measurements in solid Kr, after verifying that in Kr photodissociation is insignificant. Using near transform limited pulses of 20 fs and by measuring time delays interferometrically, the accuracy and dynamic range of the measurement is significantly improved in the present. This allows a precise characterization of the evolving vibrational coherence. We describe how a single broadband measurement allows the accurate characterization of the first six vibrations of the molecule, yielding the solvated potential and its dynamical couplings through frequencies and dephasing times.

EXPERIMENT

The measurements are carried out on thin films of I₂ isolated in solid Kr, at a doping ratio of 1:5000. Transparent films are prepared using pulsed deposition of the premixed gas from a 1-l bulb, onto a sapphire substrate held at 32 K using a closed-cycle helium cryostat. Initial backing pressures are typically between 500 and 1000 torr. The films are grown until the sample appears purple to the eye. Krypton of manufacturer’s stated purity of 99.995% (Air Gas) was used without further purification. Iodine of 99.99%+ stated purity (Aldrich Chemical), was subjected to three freeze-pump-thaw cycles to remove trapped air before use.

The femtosecond spectrometer used for collecting the TRCARS signals is shown in Fig. 1. A regeneratively amplified, diode-pumped, fiber-laser (Clark-MXR 2001) is used to pump two home-built supercontinuum seeded, noncollinear, optical parametric amplifiers (NOPA’s), which are tunable over the range of 480–650 nm. The pulses produced by the
NOPA’s carry well over 700 cm\(^{-1}\) of bandwidth (full width at half maximum) and are near transform limited with energies of 10 \(\mu J\) pulse. The output of NOPA I is split using a broadband 50/50 beam splitter to produce the pump and probe beams using a 50/50 beam splitter (BS). The same BS is used to combine the chopped He:Ne laser which traces the pump and probe beam paths, which is picked off after the translation stages (TS) using a two microscope cover slips (4\% BS). The photodiode (PD) is used for phase sensitive detection of the interference between the two legs of the He:Ne tracer. The three fs pulses are focused on the sample through the single achromat (AC), and the spatially filtered AS beam is detected using a photomultiplier (PMT), through a 3-m monochromator (M).

\(A\) - A 3-m monochromator which serves as a spectral filter. As shown in Fig. 2, the bandpass of the monochromator is significantly narrower than the AS window defined by the energy conservation condition \(\omega_{AS}=2\omega_P-\omega_S\), and obtained by the triple spectral convolution: \(I(\omega_P)\otimes I(\omega_P)\otimes I(\omega_S)\). A significant portion of the signal is rejected, primarily from the spectral distribution that overlaps the Pump and Stokes beams. This compromise is necessary, since effectiveness of the spatial filtering is limited due to light scattering in the sample. The signal is detected using a cooled photomultiplier (PMT), averaged on a boxcar integrator, digitized and stored on a personal computer. The pulse intensities are attenuated, to deliver \(\sim 100 \text{ nJ}\) over a spot size of \(\sim 35 \mu \text{m}\), comparable to the thickness of the film. The measurements are carried out at 32 K.

Although the translation stages are equipped with optical encoders capable of resolving 20-nm movement (Ealing), mechanical imperfections of the stages lead to periodic modulation of the time base (1.5\% cosine error specified), and therefore frequency modulation (FM) of the signal. The FM manifests itself as sidebands in the Fourier transformed data. An example is shown in Fig. 3, in which the stage artifact leads to evenly spaced replicas of the fundamental beats at 200 cm\(^{-1}\) with a spacing of 10 cm\(^{-1}\). To correct for this, a He:Ne laser (\(\lambda=594 \text{ nm}\)) is used to trace the pump and probe beam paths (see Fig. 1). The He:Ne beams are picked off just prior to the sample, using two glass slide cover slips and recombined after passing them through a long-pass filter. The He:Ne laser is modulated with a tuning fork chopper, and the interferometric signal is recorded using a lock-in amplifier. The interference fringes serve as an absolute time base, completely eliminating stage artifacts, as shown in Fig. 3. An absolute time-base resolution of \(\delta t\)
<0.1 fs is in principle possible \[ \delta t \sim \lambda/(2nc) \], \( n \) is the number of acquisition points per fringe, \( \lambda \) is the wavelength of the He:Ne laser, and \( c \) is the speed of light.

**RESULTS**

The observed TRCARS signal is shown in Fig. 4, on several time scales. The expansion over the first 5 ps highlights the deep modulation of the signal (>95%) at a regular period of 166 fs, given by the period of vibration of iodine in its ground electronic state \( \omega_e = 214 \text{ cm}^{-1} \) in the gas phase.\(^{28}\) This segment also reveals a gentle amplitude modulation, with a period of \( \sim 2 \text{ ps} \). Additionally, the baseline reached during the oscillations in the first 1 ps show a modulation that is absent at later time. This effect is now understood to be due to interference from TRCARS on the excited \( B \) state,\(^{29}\) and given its very minor contribution here, it will be ignored in the rest of this analysis. On the time scale of 150 ps, the envelope shaped by dephasing and rephasing of the anharmonic superposition can be observed as the signal decays. The main recursion in the envelope, of 30 ps, corresponds to the first anharmonicity of iodine in the ground electronic state \( \omega_e \sqrt{x} = 0.6127 \text{ cm}^{-1} \) in the gas phase.\(^{28}\) The detailed structure of the envelope (see, for example, the nodal region depicted by the expansion over \( t = 5–25 \text{ ps} \) in Fig. 4), is dictated by the complex amplitudes of the evolving vibrational superposition. The signal contains information out to 160 ps, i.e., the coherence can be observed for \( \sim 1000 \) vibrations of the molecule.

The spectrum of the transient is shown in Fig. 5(a). In the fundamental region, near 200 \text{ cm}^{-1}, four main peaks can be identified along with weaker shoulders on either side. These correspond to the fundamental beat frequencies, \( \omega_{p+1} - \omega_p \), split by anharmonicity. Up to the fourth beat overtone can be resolved near 1030 \text{ cm}^{-1}, which establishes that the detected vibrational superposition contains at least six vibrations. Consistent with this, two beats are seen in the third overtone region, and three beats are seen in the second overtone region. The intensities of the beats are determined by the complex vibrational amplitudes; their frequencies and widths yield the algebraic relations that determine vibrational frequencies and dephasing times. A global analysis is required for a precise characterization of the evolving coherence. The experimental time resolution is part of such an analysis. Resolving a beat frequency at 1030 \text{ cm}^{-1} establishes that the overall experimental time resolution is shorter than 30 fs. Indeed, in this measurement, the time resolution is limited by the bandpass of the monochromator (see Fig. 2) rather than the laser pulse widths. This consideration must be explicitly included in the analysis to distinguish between the prepared and observed polarization.

The magnification of the spectrum shown in Fig. 5(b) reveals a beat at 41.5 \text{ cm}^{-1}, with amplitude somewhat larger than the third overtones. Sidebands shifted by the same frequency are also discernible on the fundamental beats [see Fig. 5(b)]. These cannot be mistaken as FM. Replica sidebands on the molecular beats, but a single line at the difference frequency between central line and sideband, is a signature of amplitude modulation (AM). We have verified that the AM is absent in the He:Ne tracer beam, and this weak modulation is reproduced in repeated measurements, in different samples. It is the polarization that is modulated, sug-
gesting coupling between the chromophore and a local cage mode.

**ANALYSIS**

The data reduction is carried out along lines developed in our prior work.\(^1\) With the choice of laser colors that are resonant with the dipole allowed \(X^1\Sigma_g^+ \rightarrow B^3\Pi_u\) transition of iodine, the experiment interrogates the all-resonant molecular third-order polarization, \(P^3(t)\),\(^30\)–\(^32\)

\[
P^3(t) \approx \left( \frac{-i}{\hbar} \right)^3 \int_0^t \int_0^{t_2} \int_0^{t_1} dt_3 dt_2 dt_1 e^{-i(\omega_p-\omega_s+\omega_p)t} \times E(k_p,t_3)E(-k_s,t_2)E(k_p,t_1)R(t_1,t_2,t_3)\]

in which the three-time material response function is defined as\(^30\)

\[
R(t_1,t_2,t_3) = \text{Tr} \left[ e^{-\beta H_B(t-t_3)/\hbar} e^{iH_B(t-t_3)/\hbar} \mu_{XB} e^{-iH_B(t-t_2)/\hbar} \mu_{BX} \right] e^{-iH_B(t-t_1)/\hbar} \mu_{BX} \right].
\]

The trace is over the density of thermally occupied phonons of the bath, \(\rho_s\), and the vibrational density of the molecule, which at the cryogenic temperature of the experiment is restricted to \(|\nu=0\rangle\langle\nu=0|\) at \(t=0\).

It is useful to think of the four-wave mixing process as: preparation, evolution, and interrogation. Since the coincident pump and Stokes pulses are short with respect to characteristic periods of the lattice modes, and the radiation acts on the molecular coordinate alone, we may identify the prepared second-order coherence as

\[
|\varphi^{(2)}(t_0)\rangle\langle\varphi^{(0)}(t_0)| = |\mu_{BX}|^2 \sum_\nu \langle \nu | a_\nu | \nu \rangle \rho_\nu |\nu=0\rangle. \tag{3}
\]

Given an exact description of the radiation fields, the amplitudes \(a_\nu\) can be obtained by explicitly integrating out \(t_1\) and \(t_2\) for the one-dimensional molecular Hamiltonian. The coefficients shown in Fig. 6 were obtained assuming transform limited coincident Pump and Stokes pulses of spectral distribution shown in Fig. 2. Consistent with the Stokes shift of 250 cm\(^{-1}\), a broad Raman packet centered at \(\nu=1\) is to be expected.

Time evolution under the vibrational Hamiltonian on the ground electronic state couples the displaced oscillator with the lattice. Ignoring the 42-cm\(^{-1}\) modulation, in the standard weak-coupling limit where the bath memory decays faster than the dephasing of the system, we may trace out the bath to describe the time evolved molecular coherence:\(^30\)

\[
|\varphi^{(2)}(t)\rangle\langle\varphi^{(0)}(t)| = \text{Tr}_b \left[ e^{-iH_B t} \sum_\nu a_\nu |\nu\rangle \rho_\nu \langle\nu=0| \right] = \sum_\nu a_\nu e^{-i\omega_\nu t} e^{-\gamma_\nu t} |\nu\rangle \langle\nu=0|. \tag{4}
\]

Thus the role of the lattice is reduced to that of dephasing, with \(\gamma\) identified as the vibration dependent overall dephasing rate—the sum of pure dephasing and dissipation.

The interrogation can be regarded as a projective measurement, \(|\nu=0\rangle b_\nu\langle\nu'|\), that maps out the detection window on the molecular states; \(b_\nu = E(\omega) \delta(\omega - \omega_\nu + \gamma_\nu t)\) where \(E(\omega)\) is the convolution of the detection window and the probe field. The time resolution of the measurement can then be associated with the finite duration of the probe window \(W(t):\(^1\)

\[
P^3(t) \approx |\mu_{BX}|^4 \sum_\nu e^{-iH_B t} \int d\tau W(t-\tau) a_\nu b_\nu e^{-i(\omega_p-\omega_s-\omega_\nu)t}\]

The computed coefficients \(b_\nu\), based on the monochromator bandpass, are shown in Fig. 6. The detection limits the observable superposition to states \(\nu=1\)–\(6\).

The homodyne detected signal consists of the squared polarization, therefore

\[
S(t) \approx |\mu_{BX}|^4 \sum_{\nu,\nu'} 2c_\nu c_{\nu'} f(\omega) \cos[\omega_{\nu,\nu'} t + \phi_{\nu,\nu'}] e^{-i(\omega_p-\omega_s)(\omega_\nu+\gamma_\nu t)}. \tag{6}
\]

The signal is modulated at the difference beat, \(\omega_{\nu,\nu'} = \omega_\nu - \omega_\nu',\) with amplitudes damped by dephasing and by the frequency response \(f(\omega)\) that arises from the convolution in Eq. (5). All parameters in Eq. (6), which is the functional form used in fitting the data, are to be directly extracted from the experimental signal.

The experimental signal is fitted to Eq. (6) by iterating between the time and frequency domain files of Figs. 4 and 5. For a six-state superposition, beside the 24 variables that characterize the coherence (complex amplitudes of modulus \(c_\nu\) and phase \(\phi_\nu\); frequencies \(\omega_\nu\), dephasing rates \(\gamma_\nu\), \(f(\omega)\) is to be extracted by its values at the mean frequency of the four overtone regions. Auxiliary equations that describe the functional relations among these variables are necessary to constrain the fit. Thus:
The frequencies are related through the anharmonic expansion
\[ \omega_v = \omega_c(v + \frac{1}{2}) - \omega_c x_c(v + \frac{1}{2})^2 + \omega_c y_c(v + \frac{1}{2})^3. \]

The dephasing rates are related through the virial expansion
\[ \gamma(v) = \sum_n \gamma^{(n)} v^n. \]

The frequency response is assumed Gaussian:
\[ f(\omega) = e^{-\omega^2/\Delta^2}. \]

A detailed reproduction of the signal is possible, as illustrated in Figs. 7 and 5, with the parameter set collected in Table I. Indeed, this large parameter set is overdetermined, allowing a meaningful test of the model assumptions (7)–(9) through sensitivity analysis. We find that it is essential to include the cubic anharmonicity in Eq. (7). The sensitivity of this determination is due to the fact that the 15 peaks observed in the spectrum of Fig. 5 provide as many algebraic relations to define the three parameters in Eq. (7). It is necessary to include the quartic term in the virial expansion of dephasing rates (8), and the linear and cubic terms make negligible contribution. The extracted vibration dependence of dephasing is illustrated in Fig. 8, along with constants extracted algebraically from the linewidths in the power spectrum. The extracted response function \( f(\omega) \) is illustrated in Fig. 9. It has a time-bandwidth equivalent of 20 fs.

The faithful reproduction of the nodal pattern of the signal in time (Fig. 9), and the overtone amplitudes in the Fourier spectrum (Fig. 2), demonstrates that the amplitudes and phases of the detected polarization are well characterized. The extracted amplitudes \( c_n \) are in good agreement with the predicted moduli \( |a_n b_n| \) as shown in Fig. 6, providing a consistency check for the formulation (6). Moreover, information about the coherence of the laser pulses can be extracted from the observed relative phases \( \phi_{v n} \) among the members of the superposition. For transform limited pulses, the relative phases are principally determined by the delay between the pump and Stokes pulse. The extracted phases are consistent with a time delay of 5 fs, but to account for the phases at the wings of the vibrational packet, cubic chirp characteristic of the prism compressors must be included.

Let us now consider the 41.5-cm\(^{-1}\) modulation. Such a modulation would result if a local mode were intimately coupled to the molecular coordinate. The observations of

### TABLE I

Parameter set extracted from the fit to the signal, with confidence coefficient \( R^2 = 0.98 \). In parentheses are the standard errors associated with the last place indicated. (a) Vibrational amplitudes. (b) Relative phases. (c) Frequency response function evaluated at the mean frequencies \( \omega \) of overtones. (d) Vibration dependence of dephasing rates. (e) Molecular vibrational parameters, in the gas phase (Ref. 28): \( \omega_c = 214.57, \omega_c x_c = 0.6127, \omega_c y_c = -0.000 \, 895 \); in Ar (Ref. 27): \( \omega_c = 214.0 \pm 0.17, \omega_c x_c = 0.638 \pm 0.009 \) all in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>( c_n ) (a)</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
<th>( c_4 )</th>
<th>( c_5 )</th>
<th>( c_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(au.)</td>
<td>0.088(1)</td>
<td>0.280(1)</td>
<td>0.488(2)</td>
<td>0.305(1)</td>
<td>0.154(2)</td>
<td>0.047(2)</td>
</tr>
<tr>
<td>( \phi_{v n} ) (b)</td>
<td>( \phi_{12} )</td>
<td>( \phi_{23} )</td>
<td>( \phi_{34} )</td>
<td>( \phi_{45} )</td>
<td>( \phi_{56} )</td>
<td></td>
</tr>
<tr>
<td>(radians)</td>
<td>-0.193(3)</td>
<td>0.052(1)</td>
<td>0.199(1)</td>
<td>-0.065(2)</td>
<td>-0.345(6)</td>
<td></td>
</tr>
<tr>
<td>( f(\omega) ) (c)</td>
<td>( \omega = 200 )</td>
<td>( \omega = 400 )</td>
<td>( \omega = 600 )</td>
<td>( \omega = 800 )</td>
<td>( \omega = 1000 )</td>
<td></td>
</tr>
<tr>
<td>(au.)</td>
<td>1.000(4)</td>
<td>0.610(6)</td>
<td>0.44(1)</td>
<td>0.38(3)</td>
<td>0.24(8)</td>
<td></td>
</tr>
<tr>
<td>( \gamma^{(0)} ) (c)</td>
<td>( \gamma^{(0)} )</td>
<td>( \gamma^{(1)} )</td>
<td>( \gamma^{(2)} )</td>
<td>( \gamma^{(3)} )</td>
<td>( \gamma^{(4)} )</td>
<td>( \gamma^{(5)} )</td>
</tr>
<tr>
<td>(ps(^{-1}))</td>
<td>8.5 \times 10^{-3}</td>
<td>4.9 \times 10^{-4}</td>
<td>( \omega_c x_c )</td>
<td>( \omega_c y_c )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(cm(^{-1}))</td>
<td>211.330(2)</td>
<td>0.6523(6)</td>
<td>0.0029(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 7. Comparison between the experimental time domain signal (top) and the reconstructed signal (bottom) using parameters from Table I.

FIG. 8. Vibration dependence of dephasing rates. The curve is the quartic virial expansion of Eq. (8), with parameters collected in Table I. The points are obtained from Lorentzian fits to the fundamental peaks in the power spectrum.
symmetric sidebands flanking the fundamental, with substructure that replicates the fundamental splittings, and a single sharp line at the local mode frequency, is sufficient to identify the coupling to be linear in the lattice coordinate $q$ and quadratic in the molecular coordinate $Q$,

$$V(Q,q) = \frac{1}{2} \mu_Q \omega_Q^2 Q^2 + \frac{1}{2} \mu_q \omega_q^2 q^2 + \frac{1}{2} \Lambda Q^2 q,$$

which leads to the classical equation of motion,

$$Q(t) = Q_0 e^{i \omega_Q t} + \frac{Q_0 q_0}{\mu_Q} \left( e^{i \omega_Q t} - (\omega_Q + \omega_q)^2 + (\omega_Q - \omega_q)^2 \right).$$

The intensities, but not the frequencies, of the sidebands will be determined by the coupling strength $\Lambda$ and vibrational amplitudes $Q_0 q_0$. Without loss of generality, the quantum evolution of the prepared anharmonic vibrational superposition (4) becomes for the coupled motion

$$\langle \varphi(2)(t) | \varphi(0)(t) \rangle = \sum_v a_v e^{-i \omega_v t} [1 + \lambda^+ (\nu) e^{i \omega_q t} + \lambda^- (\nu) e^{-i \omega_q t} + \gamma |\nu\rangle\langle \nu | (\nu = 0)].$$

The observable signal, which is given by the square of the sum of the oscillating terms in Eq. (12), will now contain the quantum beats of the coupled motion. In addition to the molecular beats at $\omega_{v,\nu} = |\omega_v - \omega_\nu|$, with intensity $2 a_v a_\nu^{*}$, the power spectrum now contains the sidebands at $\omega_{v,\nu} \pm \omega_q$ with intensity $\lambda a_v a_\nu^{*} [\lambda \sim \lambda^- (\nu) \ll 1]$, and the pileup of the diagonal differences $|\omega_v - (\omega_\nu \pm \omega_q)| = \omega_q$ leads to the appearance of the cage frequency with intensity $\Sigma \lambda a_v^2 \sim n \lambda^2 \nu^2/2$ for an $n$-state superposition. Sideband overtones, shifted by $\pm 2 \omega_q$, would have amplitudes reduced by $\lambda^2$—too small to be observable. Ignoring its dependence on vibrational amplitude, using a coupling constant $\lambda (\nu) = \lambda = 0.01$ independent of vibrational amplitude of the chromophore, the sidebands are adequately reproduced within S:N limitations, as illustrated in Fig. 5(b). This treatment overestimates the amplitude of the cage mode [see Fig. 5(b)].

The inclusion of a $\nu$-dependent coupling could in principle remedy this. The fit yields a precise determination of the cage frequency: $\omega_q = 41.56 \pm 0.03 \text{ cm}^{-1}$, with linewidth strictly determined by the dephasing time of the molecular coherence. It is also noteworthy that the cage modulation in the time file appears as $\cos(\omega_q t + \phi)$ with $\phi = 0$, establishing that it starts from its equilibrium position. This suggests that the cage mode is driven by a momentum kick imparted during the preparation of the Raman packet.

**DISCUSSION**

TRCARS measurements of iodine have previously been carried out in the gas phase. Due to the elimination of rotations, the signal in the matrix is simplified to a strict measurement of vibrational coherence on the ground electronic state. Moreover, the fast electronic dephasing in the matrix acts as a momentum filter that eliminates the period doubling observable in TRCARS measurements in the gas phase. This, along with the use of short laser pulses, leads to a time resolved signal with $\sim 100\%$ depth of modulation. Moreover, the weak coupling between I$_2$ and the Kr lattice leads to a long-lived coherence. As a result, the TRCARS signal in the matrix is more sharply defined than in the gas phase, and its extensive recursions allow a precise analysis of the material coherence and radiation fields used. A wealth of information is extracted through a careful analysis of a single measurement, as detailed in the prior section.

An important aim of this work is to provide precise experimental data on the model system of matrix isolated iodine. The most basic of these is the description of the solvated molecular potential, characterized through its modified vibrational parameters. The present time domain measurements improve the vibrational resolution by nearly two orders of magnitude over the prior frequency domain data. Although less precisely measured in Ar than in Kr is positive, as opposed to the gas phase where it is negatively modulated. Evidently, in the bi-substitutional site of Kr, the molecule is subject to a net tensile stress. This arises from the interplay of an attractive axial force and a repulsive force along the belt where the fit is tight. The same general considerations determine the modified anharmonicities. Note, the cubic anharmonicity in Kr is positive, as opposed to the gas phase where it is negative (see Table I). In effect, the cage wall is felt even in the low-lying states. It would be interesting to test whether the observed vibrational parameters can be reproduced using the various anisotropic pair interactions for I-Rg, and whether nonadditivities of interactions play a discernible role.

The coupling between the guest and host is revealed through the vibration dependent dephasing rates. In this regard, it is worth noting that there is no evidence of inhomogeneous broadening in the data, the signal is strictly fit as the sum of decaying exponentials, or equivalently, the Fourier spectrum reveals Lorentzian lines. The observed dephasing time of $\nu = 1$ in Kr is nearly one order of magnitude longer than in Ar. Qualitatively, this may be ascribed to the fact that...
in Ar the isolation site is tight, and therefore the molecule samples the repulsive wall of the cage potential as it vibrates. The vibration dependence of dephasing rates in the two matrices has notable differences. In Kr we observe a strong \( \nu \) dependence, see Fig. 8, dominated by the even powers in \( \nu \) (see Table I). In Ar, the dependence is weaker and, within the sizable errors of the measurement, the dependence is nearly linear for \( \nu \approx 1-12 \).\(^{27}\) Presumably, these reflect the interaction potential dynamically sampled as the molecule vibrates in its trapping site. The qualitative inference may be that while in the tight site of Ar the molecule samples the repulsive wall of the cage, in the looser site in Kr, the molecule samples a potential which is relatively flat, locally quadratic and quartic. It would be interesting to see if these findings are borne out in quantitative treatments of dephasing, whether known potentials have the accuracy to reproduce the dynamics.

The surprising finding in the present measurement is the 41.5 cm\(^{-1}\) modulation, which can be consistently analyzed as arising from a local mode coupled to the molecular coordinate. The analysis is also consistent with this mode being impulsively driven during the preparation of the molecular vibrational superposition, during the electronic coherence limited to the width of the laser pulse of 20 fs. The impulse that drives the local mode must be limited to a momentum kick upon suddenly switching the electronic potential from that drives the local mode must be limited to a momentum.

Similarly, the extent of localization of a mode on the immediate cage, \( \zeta(20) \), may be defined by running the sum in the numerator of Eq. (13) over the I atoms and their 18 nearest neighbors. Since there are 108 atoms in the cell, for a mode equally distributed on all atoms, \( \zeta(20) \approx 18.5\% \) and \( \zeta(I_2) = 1.85\% \) would be expected. In Table II we provide a decomposition for selected modes. Beside the extent of localization on the molecule and the cage, we identify the nature of the molecular motion as stretch \( (\nu) \), center of mass \( (\text{cm}) \), or libration \( (\text{lib}) \). The cage amplitude is further decomposed into the four different classes of nearest neighbors identified by their orientation relative to the molecular axis;\(^{26}\) 90° refers to the belt atoms, of which there are four; 0° refers to the axial atoms, of which there are two; there are eight cage atoms at 30° and four at 60°.

Let us highlight the information in Table II. The molecular vibration, at 211 cm\(^{-1}\), which is a pure stretch, shows a localization of \( \zeta(I_2) = 97\% \). The next two modes with highest degree of localization on \( I_2 \), \( \zeta(I_2) \sim 10\% \), are principally molecular center-of-mass motions driven by the belt mode. Mode 265, at 15.79 cm\(^{-1}\), is an acoustic phonon that drives the center of mass of the molecule with \( \zeta(I_2) = 9.2\% \), but \( \zeta(20) = 21.1\% \) indicating that this mode is fully delocalized over the cell. The same applies for mode 238. The molecular librational modes 105 and 109 near 34 cm\(^{-1}\) show significant amplitude on the molecule, 4% and 6%, respectively, but the rest of the mode is fairly distributed over the lattice. In all other modes the localization on the molecular center is less than 4%. All modes that appear above the Debye limit of 49 cm\(^{-1}\) show cage localization, \( \zeta(20) > 40\% \), and significant participation by the belt atoms. The blueshift of these modes out of the Debye limit is due to the repulsive interaction between the molecule and the belt atoms—the molecule is pinched around its belt. All modes below 45 cm\(^{-1}\) are fairly delocalized, with \( \zeta(20) \approx 30\% \). We have canvassed for the appearance of large amplitude on given cage modes, but this

| Table II: Decomposition of normal mode amplitudes. The table gives a breakdown for selected normal modes in terms of: frequency [\( \omega \)], % localization on the molecule \( \zeta(I_2) \) and on the local site consisting of the molecule and its 18 nearest neighbors (\( n \)), the nature of the molecular motion based on its extent of vibration [\( \nu \)], center-of-mass motion [\( \text{cm} \)], or libration [\( \text{lib} \)], and the breakdown of the vibrational amplitude on a given nearest-neighbor atom belonging to one of the four classes identified by the angle they span relative to the molecular axis. |

<table>
<thead>
<tr>
<th>No.</th>
<th>( \omega ) (cm(^{-1}))</th>
<th>( \zeta(I_2) )</th>
<th>( \zeta(20) )</th>
<th>( \nu )</th>
<th>c.m.</th>
<th>lib</th>
<th>0°</th>
<th>30°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>211.00</td>
<td>97.0</td>
<td>99.8</td>
<td>99.5</td>
<td>0.0</td>
<td>0.5</td>
<td>0.04</td>
<td>0.21</td>
<td>0.04</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>59.07</td>
<td>12.2</td>
<td>51.7</td>
<td>0.2</td>
<td>98.4</td>
<td>1.5</td>
<td>0.09</td>
<td>0.79</td>
<td>0.17</td>
<td>8.71</td>
</tr>
<tr>
<td>3</td>
<td>57.46</td>
<td>9.4</td>
<td>48.5</td>
<td>1.3</td>
<td>97.1</td>
<td>1.6</td>
<td>0.06</td>
<td>0.70</td>
<td>0.71</td>
<td>7.64</td>
</tr>
<tr>
<td>4</td>
<td>55.56</td>
<td>3.3</td>
<td>39.6</td>
<td>5.9</td>
<td>73.4</td>
<td>20.7</td>
<td>0.10</td>
<td>0.54</td>
<td>0.24</td>
<td>7.99</td>
</tr>
<tr>
<td>5</td>
<td>55.31</td>
<td>2.3</td>
<td>39.1</td>
<td>10.3</td>
<td>68.4</td>
<td>21.2</td>
<td>0.10</td>
<td>0.64</td>
<td>0.26</td>
<td>7.99</td>
</tr>
<tr>
<td>6</td>
<td>51.97</td>
<td>3.7</td>
<td>45.1</td>
<td>3.7</td>
<td>26.1</td>
<td>70.2</td>
<td>1.55</td>
<td>4.22</td>
<td>0.39</td>
<td>4.55</td>
</tr>
<tr>
<td>7</td>
<td>51.66</td>
<td>4.9</td>
<td>47.9</td>
<td>0.3</td>
<td>1.7</td>
<td>98.0</td>
<td>1.42</td>
<td>4.17</td>
<td>0.68</td>
<td>4.53</td>
</tr>
<tr>
<td>8</td>
<td>50.83</td>
<td>2.3</td>
<td>46.8</td>
<td>0.3</td>
<td>26.7</td>
<td>73.0</td>
<td>0.94</td>
<td>4.75</td>
<td>0.45</td>
<td>4.99</td>
</tr>
<tr>
<td>9</td>
<td>49.08</td>
<td>3.8</td>
<td>41.3</td>
<td>1.5</td>
<td>35.0</td>
<td>63.5</td>
<td>1.09</td>
<td>2.93</td>
<td>1.14</td>
<td>3.62</td>
</tr>
<tr>
<td>10</td>
<td>48.98</td>
<td>2.9</td>
<td>38.7</td>
<td>0.7</td>
<td>12.7</td>
<td>86.6</td>
<td>0.80</td>
<td>2.69</td>
<td>1.20</td>
<td>3.47</td>
</tr>
<tr>
<td>11</td>
<td>44.81</td>
<td>3.9</td>
<td>33.7</td>
<td>0.1</td>
<td>1.7</td>
<td>99.2</td>
<td>1.33</td>
<td>3.00</td>
<td>1.18</td>
<td>1.43</td>
</tr>
<tr>
<td>12</td>
<td>46.38</td>
<td>3.8</td>
<td>30.5</td>
<td>0.2</td>
<td>4.1</td>
<td>95.7</td>
<td>0.93</td>
<td>2.03</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>13</td>
<td>45.17</td>
<td>4.2</td>
<td>32.6</td>
<td>2.2</td>
<td>52.6</td>
<td>45.1</td>
<td>2.34</td>
<td>3.54</td>
<td>1.05</td>
<td>0.73</td>
</tr>
<tr>
<td>14</td>
<td>35.24</td>
<td>4.1</td>
<td>22.7</td>
<td>2.0</td>
<td>4.5</td>
<td>93.5</td>
<td>0.72</td>
<td>2.35</td>
<td>0.53</td>
<td>0.90</td>
</tr>
<tr>
<td>15</td>
<td>33.55</td>
<td>6.3</td>
<td>21.7</td>
<td>1.9</td>
<td>2.5</td>
<td>95.6</td>
<td>1.23</td>
<td>1.52</td>
<td>0.51</td>
<td>0.70</td>
</tr>
<tr>
<td>16</td>
<td>23.83</td>
<td>4.2</td>
<td>19.0</td>
<td>0.0</td>
<td>0.8</td>
<td>98.2</td>
<td>1.17</td>
<td>0.71</td>
<td>0.45</td>
<td>0.71</td>
</tr>
<tr>
<td>17</td>
<td>16.59</td>
<td>9.2</td>
<td>21.1</td>
<td>0.0</td>
<td>0.9</td>
<td>95.9</td>
<td>0.40</td>
<td>1.30</td>
<td>0.32</td>
<td>0.80</td>
</tr>
</tbody>
</table>
CONCLUSIONS

TRCARS measurements with broadband, short laser pulses lend themselves to a detailed analysis of prepared and interrogated coherences in condensed phase, yielding a precise characterization of not only the system but also the fields employed. A single measurement, in which a six-state vibrational superposition is prepared, has served to characterize the equilibrium and dynamic interactions of the model system of I$_2$ doped matrix Kr with unprecedented precision and detail. The solvated potential of the molecule in the ground electronic state is now characterized up to cubic anharmonicity, with precision comparable to that of the gas phase. The dynamical coupling between chromophore and lattice is characterized in terms of dephasing rates of $\nu=1$–6, showing a strong $\nu$ dependence. The long coherence time of $10^3$ vibrational periods of motion of the molecule is what allows the precise definition of these parameters. The weak coupling between chromophore and lattice implies that the bath memory decays faster than the dephasing time of the chromophore, and therefore dynamics of the bath is not directly observable. One local mode defies this generalization. We observe a cage-molecule mode at 41.5 cm$^{-1}$, which rings without evidence of dephasing for times as long as 100 ps. This finding is quite surprising since the mode is resonant with the lattice phonons, yet it must remain mechanically decoupled from the bath. Consideration of the forces and interactions can be used to suggest a motion, such as the wobble of the molecule as it vibrates with its waist pinched by the belt atoms. Yet, normal modes calculated with approximate pair parameters do not reveal any localized resonant modes.

ACKNOWLEDGMENTS

This research was made possible through a grant from the US AFOSR (Grant No. F49620-01-1-0449), for which we are grateful. We thank T. Kumada for his contribution to data analysis.