Probing the structure and dynamics of molecular clusters using rotational wavepackets

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The chemical and physical properties of molecular clusters can heavily depend on their size, which makes them very attractive for the design of new materials with tailored properties. Deriving the structure and dynamics of clusters is therefore of major interest in science. Weakly bound clusters can be studied using conventional spectroscopic techniques, but the number of lines observed is often too small for a comprehensive structural analysis. Impulsive alignment generates rotational wavepackets, which provides simultaneous information on structure and dynamics, as has been demonstrated successfully for isolated molecules [1–8]. Here, we apply this technique for the first time to clusters comprising of a molecule and a single helium atom. By forcing the population of high rotational levels in intense laser fields we demonstrate the generation of rich rotational line spectra for this system, establishing the highly delocalised structure and the coherence of rotational wavepacket propagation. Our findings enable studies of clusters of different sizes and complexity as well as incipient superfluidity effects using wavepacket methods.

The study of weakly bound clusters requires very low temperatures to allow their formation, implying the population of only the lowest quantum levels. Consequently, the features in conventional rotational microwave (MW) spectroscopy comprise only a few lines – often not enough for a comprehensive analysis of the structure [9]. In contrast, spectral features of variable complexity can be generated using impulsive alignment. In this method, a rotational wavepacket forms through the non-resonant interaction of an intense laser field with a molecule, aligning it in space [10]. Tuning the laser pulse duration and intensity controls the number of rotational eigenstates in the wavepackets. By following the evolution of alignment in time it is possible to map these eigenstates and explore the rotational dynamics. Given the equivalence of time and frequency-domain information, spectra comprising of few, or many, lines can be generated. This ability is also of advantage for the exploration of liquids where the wavepacket dynamics will be sensitive to dephasing. A particularly promising liquid to begin such studies is superfluid helium. Frequency-domain spectra of molecules embedded into large superfluid helium droplets show sharp rotational transitions, suggesting that wavepackets will not dephase [9, 10]. However, the recent attempt to impulsively align molecules in large helium droplets by Pentelechner et al. showed that this was not the case [11]. The findings remain unexplained.

This work was motivated to establish a bridge between free molecules and helium droplets. We chose to study clusters of acetylene (C$_2$H$_2$) and a single helium atom in order to reduce size and complexity to a minimum. Rotational spectroscopy (MW) of C$_2$H$_2$ has neither been performed in large helium droplets nor in small clusters before, one limitation being a lack of a permanent dipole moment needed in MW spectroscopy. Several potential energy surfaces for C$_2$H$_2$–He nevertheless exist, allowing for comparison between experiment and theory [12–14].

A beam comprising small C$_2$H$_2$–He clusters was generated in a pulsed, supersonic expansion and propagated through a vacuum apparatus [15]. To excite rotational wavepackets 300 fs laser pulses (pump) intersected the beam of clusters followed by 50 fs laser pulses (probe) to detect molecular alignment (Fig. 1). Control of the number of rotational levels excited in the wavepackets was achieved by variation of the intensity of the pump pulses between $5 \times 10^{11}$ and $5 \times 10^{12}$ W cm$^{-2}$. The probe pulse had a constant intensity of $1 \times 10^{15}$ W cm$^{-2}$, sufficient to instantly break molecular bonds in a Coulomb explosion, thereby generating C$^+$ fragment ions. Their velocity vectors, carrying the molecular alignment information, were selectively detected in a velocity map imaging (VMI) spectrometer [16] whose detector plane was parallel to the polarisation plane of both laser beams (xy plane in Fig. 1). The two-dimensional projection of the recoiling C$^+$ fragment directions and intensities was used to determine $\cos^2(\theta)$ for each position on the detector, where $\theta$ designates the angle between polarisation of the pump laser and the projected velocity vectors. The average over the entire detector area, $\langle \cos^2(\theta)_{2D} \rangle$, is propor-
Helium-C\(_2\)H\(_2\) clusters produced by expansion of 0.01 % C\(_2\)H\(_2\) in 7 MPa He through a cooled Even-Lavie valve were irradiated by femtosecond pulses originating from a 30 fs, 1 kHz Ti:Sapphire laser operating at 800 nm (KM Labs Red Dragon). Both, pump and probe laser beams, comprising of separate grating compressors (not shown), were colinearly focused through a \(f = 500\) mm lens into the molecular beam 50 mm downstream from the nozzle exit.

This parameter was measured as a function of time by scanning the delay between pump and probe laser pulses to reveal the rotational dynamics of the clusters.

Fig. 2 shows raw Coulomb explosion images for C\(^+\) under different expansion conditions. Fig. 2(a) shows the ion image under conditions where free C\(_2\)H\(_2\) (no helium attached) is the dominant molecular species in the expanding gas. This particular image shows relatively sharp features, with evidence of more than one fragmentation channel leading to the formation of C\(^+\). By way of contrast, Fig. 2(b) shows the image obtained when the nozzle was cooled to 203 K to facilitate the formation of clusters. The angular distribution of the two images is identical, the only difference being higher kinetic energies in image (b). Increased kinetic energy unambiguously indicates the generation of further charges, although the laser parameters themselves have not changed. Space-charge effects can be excluded given that the temperature variation increases the gas number density in the interaction region only by 30 % – an insignificant reduction in the internuclear separation of ions in the gas compared to the high atomic number density within a cluster. We suspect that a mechanism, similar to that predicted for large helium droplets doped with Xe atoms, is operating for small clusters \cite{17}. In our case the ionisation probability of He atoms might be enhanced by the presence of the solvated molecule.

The time-resolved molecular alignment, \((\cos^2(\theta)_{2D})\), is shown in Fig. 3 for conditions similar to Fig. 2(b). The strongest contribution originates from C\(_2\)H\(_2\) whose full, half and quarter revivals reappear every rotational period as maximum alignment and anti-alignment. The features extend over the full range of the scan up to 600 ps without any appreciable decay in amplitude or shape, so one can infer that the coherence of the rotational wavepacket is at least 600 ps. Acetylene-helium cluster (C\(_2\)H\(_2\)-He\(_n\)) revivals are difficult to directly identify in the alignment scan. Therefore, a Fourier transform is performed, providing a much clearer picture.

\begin{figure}[H]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Schematic of experimental setup.}
\end{figure}

\begin{figure}[H]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Velocity map images.}
\end{figure}

\begin{figure}[H]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Time-resolved alignment. (a) Rotational revivals obtained under conditions where the helium stagnation pressure and temperature were 6.4 MPa and 217 K, respectively. Note that the baseline has been subtracted. The data has been smoothed. The time difference between two full revivals is equal to the rotational period of acetylene and is indicated by a double-headed arrow. (b) For time delays up to the maximum of 600 ps, no decay in the amplitude, nor in the shape of the revivals, was observed. The coherence time of the wavepacket for free C\(_2\)H\(_2\) molecules is therefore at least 600 ps.}
\end{figure}
The Fourier transform of the time-resolved molecular alignment is shown for two different pump laser intensities in Fig. 4(a). A series of discrete lines is produced, which corresponds to particular frequency contributions of C$_2$H$_2$ to the rotational wavepacket. The strongest features seen in Fig. 4(a) coincide with the beat frequencies of C$_2$H$_2$ at $6B + 4nB$, where $B$ is the C$_2$H$_2$ rotational constant ($B = 1.1769$ cm$^{-1}$) and $n = 0$, 1, 2, 3, etc. Six members of this series are seen at the pump power of $5 \times 10^{11}$ Wcm$^{-2}$. The first line at $6B$ frequency is equivalent to the $J' = 2 \leftarrow J'' = 0$ transition, with successive lines at $10B$, $14B$, $18B$, etc. When the pump laser intensity is increased to $5 \times 10^{12}$ Wcm$^{-2}$, higher rotational transitions are induced, reaching up to the $J = 13$ rotational energy level.

In the low frequency range, shown in Fig. 4(b), several prominent peaks were observed which do not fit to the well-known rotational transitions for free C$_2$H$_2$ and are therefore attributed to C$_2$H$_2$-He$_n$ clusters. The full widths at half maximum of these features were found to be 0.03 cm$^{-1}$, which matches the experimental limit in resolution set by the length of the delay scan of 600 ps. Hence, the line width of the peaks assigned to C$_2$H$_2$-He$_n$ clusters is consistent with a coherence time for the rotational wavepacket of at least 600 ps. This first observation of coherent propagation of rotational wavepackets in small C$_2$H$_2$-He$_n$ clusters contrasts with the strong dephasing found in large helium droplets. As detailed below we can assign some of the C$_2$H$_2$-He$_n$ features to the simplest cluster, C$_2$H$_2$-He.

To guide the assignment the interaction energies for this cluster were calculated over a wide range of structures using the coupled cluster singles and doubles with perturbative triples (CCSD(T)) method. The analytical potential energy surface was used to compute rotational energy levels and wave functions, as detailed in the supplementary information. Selected levels and transition energies from these calculations are displayed in Fig. 6 and collected in Table I. The computed rovibrational ground state energy is -7.417 cm$^{-1}$ relative to the dissociation limit into C$_2$H$_2$ + He. Only the total angular momentum quantum number $J$ and the parity of the wave functions are rigorous quantum numbers. Parity is coded by the symbols $e$ and $f$ for levels with parity $(-1)^J$ and $(-1)^J$, respectively. Inspection of the level structure and analysis of the wave functions reveals that the C$_2$H$_2$-He does not behave like a linear molecule in$\ldots$
FIG. 6. Rotational energy level diagram of C$_2$H$_2$-He. The vertical arrows designate the transitions observed, whereas the dashed, grey arrows indicate possible but not observed transitions.

TABLE I. Energy level assignment of measured lines. Quantum numbers of the initial states are denoted by $j''$, $K''$, $J''$ and of the final states by $j'$, $K'$, $J'$. The experimental line positions are given in cm$^{-1}$ and the estimated error margin in each case is $\pm 0.03$ cm$^{-1}$. The transition labels in the first column are identical with the labels of the peaks in Fig. 5.

| Label | Sym. | $j''$ | $K''$ | $J''$ | $j'$ | $K'$ | $J'$ | Exp. | Calc. |
|-------|------|-------|-------|-------|------|------|------|------|-------|
| 1     | $e$  | 1     | 0     | 0     | 1    | 0    | 2    | 0.58 | 0.60  |
| 3     | $e$  | 1     | 0     | 1     | 1    | 0    | 3    | 1.51 | 1.49  |
| 4     | $e$  | 1     | 0     | 2     | 1    | 0    | 4    | 2.41 | 2.41  |
| 2     | $e$  | 0     | 0     | 0     | 0    | 0    | 2    | 1.43 | 1.46  |
| 4     | $e$  | 0     | 0     | 1     | 0    | 0    | 3    | 2.41 | 2.40  |
| 5     | $f$  | 1     | 1     | 1     | 1    | 1    | 3    | 2.50 | 2.50  |

Based on these results, five peaks at 0.58, 1.43, 1.51, 2.41 and 2.50 cm$^{-1}$ were assigned to C$_2$H$_2$-He, yielding an agreement between theory and experiment within 0.02 cm$^{-1}$. We note that the present calculation provides a better match to the measured line positions than the best potential energy surface available prior to this work. The expected Raman transitions for C$_2$H$_2$-He are marked in Fig. 5 by vertical arrows and text, showing the energy differences in cm$^{-1}$. The assignment of the lines in the low frequency range is shown in Table I.

The identified C$_2$H$_2$-He features depend distinctly on the pump laser intensity as shown in Figs. 5(b) and (c). At lower pump intensity, two lines exceed the noise level, namely the lines assigned to the transitions $J' = 2 \leftrightarrow J'' = 0$ in the $j = 1$, $K = 0$, $e$ manifold, labelled '1', and the $J' = 3 \leftrightarrow J'' = 1$ in the $j = 1$, $K = 1$, $f$ manifold, labelled '5'. The intensities of these lines grow with increasing pump laser energy due to more clusters being excited. Additional lines emerge, for example the $J' = 2 \leftrightarrow J'' = 0$ transition in the $j = 0$, $K = 0$, $e$ manifold, labelled '2'. Population transfer to higher lying states in the rotational wavepacket due to more intense pumping is also observed. In particular, the $J'' = 2$ state in the $j = 1$, $K = 0$, $e$ manifold is pumped to the $J' = 4$ state, labelled '4'. Two further transitions, the $J' = 5 \leftrightarrow J'' = 3$ in the $j = 1$, $K = 0$, $e$ and the $J' = 5 \leftrightarrow J'' = 3$ in the $j = 0$, $K = 0$, $e$ manifold, indicated in Fig. 5(a) by dotted arrows, exhibit intensities within the noise level and cannot safely be established.

In conclusion, it has been shown for the first time that it is possible to construct a coherent rotational wavepacket for a weakly bound cluster between a molecule and a helium atom using impulsive alignment. The dynamics of this wavepacket was followed in the time domain using a second laser pulse, yielding features that can be subjected to Fourier transformation to yield the underlying rotational energy level structure. By this means we have established the highly delocalised, floppy structure of C$_2$H$_2$-He, a van der Waals cluster which is only bound by ca. 7 cm$^{-1}$. The observed rotational energy level structure is in excellent agreement with theoretical predictions.

Our observation enables the simultaneous determination of structure and dynamics in free atomic and molecular clusters, which is vital for the fundamental understanding of size-effects and interactions in condensed matter, for example, incipient superfluidity. This knowledge will ultimately be critical for the development of new materials with tailored properties, addressing the relevance of clusters in various applied disciplines, for example catalysis, solar cells, opto-electronics and biomedical imaging.

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Supplementary information: 
Prediction of rovibrational states of $\text{C}_2\text{H}_2$-$\text{He}$

The $\text{C}_2\text{H}_2$ unit was fixed at its experimental ground state averaged geometry. The interaction energies between $\text{C}_2\text{H}_2$ and a helium atom were computed in a Jacobi coordinate system with a Jacobi vector $R$ pointing from the centre of mass of $\text{C}_2\text{H}_2$ to the helium atom and a Jacobi angle $\theta$ enclosed between $R$ and the $\text{C}_2\text{H}_2$ molecular axis. Total electronic energies were computed on a grid of 300 points covering $0 \leq \theta \leq 90^\circ$ in steps of $10^\circ$ and a $\theta$ dependent radial grid typically ranging between 2.50 and 20 Å. We used the coupled cluster singles and doubles with perturbative triples, CCSD(T), method and included all 16 electrons in the correlation treatment. Core optimised correlation consistent augmented (doubly augmented for He) basis sets according to Dunning were employed as implemented in the MOLPRO electronic structure package. Total energies for the complex obtained with basis sets from triple zeta, (d)aug-cc-pCVTZ, to quintuple zeta, (d)aug-cc-pCV5Z, were extrapolated to the complete basis limit using the procedure of Peterson et al. The extrapolated total energies were converted into interaction energies by subtracting the result of an extrapolation for tal energies were converted into interaction energies by the procedure of Peterson et al. and a Jacobi angle $\theta$ equal to 0. The grid point with the strongest interaction between $\text{C}_2\text{H}_2$ and a helium atom were computed in a Jacobi coordinate and a distributed Gaussian basis (DGB) for the radial degree of freedom. We used 51 Gauss-Legendre DVR points in $\theta$ and an angle dependent radial basis composed of up to 85 non-evenly distributed Gaussians between 2.1 and 160 Å. Energy eigenvalues and wave functions were computed for both parities and for total angular momentum $0 \leq J \leq 10$, but only levels up to $J = 5$ were found to be bound. Energy levels are converged to better than 0.001 cm$^{-1}$. The computed rovibrational ground state energy is -7.417 cm$^{-1}$. The computed level structure and the analysis of the wave functions shows that $\text{C}_2\text{H}_2$-$\text{He}$ does not behave like a linear molecule in spite of its linear electronic minimum. Already in its rovibrational ground state the complex is completely delocalised over the entire angular domain.

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