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# Gas-phase vibrational spectroscopy of the dysprosium monoxide molecule and its cation

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Rotationally resolved vibrational spectra of DyO and DyO<sup>+</sup> in a molecular beam are obtained by IR excitation from the X8 ground state and from high-*n* Rydberg states of DyO using an infrared free electron laser. Vibrational excitation is detected either by resonance enhanced multiphoton ionisation from X8(*v* = 1) or by autoionisation of Rydberg states converging to DyO<sup>+</sup>(*v* = 1). For most heavy molecules, the large spectral width of an infrared free electron laser does not allow for rotational resolution. In DyO and DyO<sup>+</sup> the P, Q, and R transitions can be resolved due to the high angular momentum in their ground states. For <sup>164</sup>DyO a vibrational constant of  $\omega_e = 847.5(2) \text{ cm}^{-1}$  and a vibrational anharmonicity of  $\omega_e x_e = 2.9(1) \text{ cm}^{-1}$  are deduced. For the <sup>161</sup>DyO<sup>+</sup> cation a transition frequency of  $\Delta G_{1/2} = 907(1) \text{ cm}^{-1}$  is found.

## Introduction

The elements within the lanthanoid series are characterised by a successive filling of the 4f shell starting with one electron for cerium up to 14 electrons for ytterbium. Their open 4f shell and energetically low-lying excitations generally can lead to extremely rich and complicated electronic spectra. Recently, related to significant developments in experimental and theoretical methods, there has been a renaissance in the studies and the understanding of isolated, lanthanoid atom containing small molecules.<sup>1–5</sup> In part, this is also related to the finding of interesting thermochemical properties, *e.g.*, for the lanthanoid monoxides, LnO, see below.<sup>6</sup>

The isolated dysprosium monoxide molecule, DyO, has been intensively studied experimentally, *e.g.*, in the gas phase by emission and absorption spectroscopy,<sup>7,8</sup> using spectrally dispersed laser induced fluorescence spectroscopy of an effusive DyO oven beam<sup>9,10</sup> or Stark effect measurements.<sup>11</sup> The thermodynamics of DyO (and DyO<sup>+</sup>) has attracted particular interest during the search for molecules with the more unusual property that their ionisation energies are below the ground-state bond dissociation energies.<sup>6,12</sup> Furthermore, the vibrational properties of DyO and its ions have been studied using cryogenic matrix isolation IR spectroscopy.<sup>13–15</sup> Knowledge on the vibrational properties of lanthanoid monoxides has led to rather fundamental insights into the electronic structure of these molecules and related species.<sup>16</sup>

The low-lying electronic states of DyO are described in ligand field theory as resulting from the states of the Dy<sup>2+</sup>

ion, perturbed by the closed-shell O<sup>2–</sup> ligand.<sup>16–18</sup> The ground state of DyO originates from the [Xe](4f<sup>9</sup>(<sup>6</sup>H)6s) configuration of Dy<sup>2+</sup>.<sup>17</sup> The lowest state of the 4f<sup>9</sup> core is <sup>6</sup>H<sub>7.5</sub>. The angular momentum *J*<sub>c</sub> = 7.5 of the core couples with the 6s electron to give a pair of states, split by the exchange interaction, with total atomic angular momentum *J*<sub>a</sub> = 8 and 7. As the 4f shell is more than half filled, the *J*<sub>a</sub> = 8 level is the lowest in energy. The interaction with the O<sup>2–</sup> ligand quantizes the projections of each *J*<sub>a</sub> state of Dy<sup>2+</sup> on the internuclear axis to give  $\Omega = J_a, J_a - 1, \dots, 0$ . The state with  $\Omega = J_a$  is the lowest in energy, and the ground state of DyO thus has  $\Omega = 8$ .<sup>9</sup> It is referred to as the X8 state and the lowest rotational level has a total angular momentum of *J* =  $\Omega$  = 8. The X8 state is closest to a <sup>7</sup>H<sub>8</sub> state,<sup>9</sup> *i.e.* with total electron spin *S* = 3 and total electron angular momentum *L* = 5, even though only  $\Omega$ , the sum of the projections of *L* and *S* on the internuclear axis, is well-defined. The removal of one electron results in  $\Omega = 7.5$ , and thus in a lowest rotational level with *J* = 7.5 for the <sup>6</sup>H<sub>7.5</sub> ground state of DyO<sup>+</sup> which can be described as Dy<sup>3+</sup>(4f<sup>9</sup>(<sup>6</sup>H))O<sup>2–</sup>.<sup>19</sup> Ghiasee *et al.* use an alternative, nevertheless equivalent, description as Dy<sup>+</sup>(<sup>6</sup>I)O(<sup>3</sup>P), see the ESI of ref. 12.

Recently, we have started gas-phase spectroscopic studies of DyO embedded in a supersonic molecular beam using several variants of laser-based ionisation techniques to obtain mass resolved excitation spectra with rotational resolution. This allowed the characterisation of new electronically excited states, the identification of several Rydberg series as well as accurate measurements of the ionisation energy, bond dissociation energy of DyO and the rotational constant of DyO<sup>+</sup>.<sup>20</sup> We report here on our study of the rotationally resolved vibrational spectra of DyO and DyO<sup>+</sup>, using excitation with a tunable

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infrared free electron laser (IR-FEL) in combination with sensitive ionisation detection schemes.

The motivation for the IR spectroscopic study of neutral DyO was in part to characterise the absolute frequency and spectral profile of the light emitted by the IR-FEL operated at the Fritz Haber institute (FHI-FEL)<sup>21</sup> using well-known molecular transitions. After having characterised the IR-FEL radiation, we have applied infrared photoinduced Rydberg ionisation (IR-PIRI) using the FHI-FEL to obtain rovibrational spectra of DyO<sup>+</sup>.

## Experimental methods

The experiments on DyO are performed in a molecular beam machine<sup>22</sup> that is coupled to the beamline of the FHI-FEL. The experimental setup includes two pulsed dye lasers that allow for the preparation and detection of DyO in different electronic states with rotational resolution, as well as a Nd:YAG laser with 4th harmonics unit that can be used for non-resonant ionisation. The experiment runs at 10 Hz repetition rate, while the FHI-FEL may also be operated at half that rate for subsequent on/off measurements.

In a laser ablation source, a rotating and translating dysprosium target (MaTeck, 6.35 mm diameter rod) is vaporized by the second harmonic output of a pulsed Nd:YAG laser (Continuum Minilite II, 2–5 mJ per pulse). In the presence of an Ar gas pulse seeded with  $\sim 0.2\%$  O<sub>2</sub> the DyO molecules are formed. Upon supersonically expanding in vacuum through a 1 mm diameter nozzle, the DyO molecules get cooled down to a rotational temperature of about 20 K. The thus formed molecular beam is shaped by a skimmer (3 mm diameter) and charged species are deflected out of the beam by the electric field (800 V cm<sup>-1</sup>) of a pair of electrodes.

The molecular beam enters the extraction region of a time-of-flight mass spectrometer (Jordan TOF Products, Inc.) that can be run either in linear or reflectron mode. In the linear configuration, the use of a small separation field of typically 1–5 V cm<sup>-1</sup> in combination with time-delayed pulsed field ionisation in a field of 100–300 V cm<sup>-1</sup>, allows to distinguish between prompt and delayed ions in a mass analysed threshold ionization (MATI) configuration.<sup>23</sup> Different resonance enhanced multiphoton ionisation (REMPI) schemes have been used to either detect the population of selected rotational levels of X8( $v = 1$ ) or to prepare DyO in Rydberg states  $n(J)$  of different principal quantum number  $n$ , in series that converge to different rotational levels  $J$  in the cation. The spectroscopy in the X8 ground state is performed using the most abundant isotopologue, <sup>164</sup>Dy<sup>16</sup>O, while the preparation of Rydberg states makes use of a resonant two-color excitation step that has been identified specifically for <sup>161</sup>Dy<sup>16</sup>O, see ref. 20.

Laser pulses in the visible region of the spectrum (about 5 ns duration) are produced by dye lasers (Sirah PrecisionScan and Radiant Dyes NarrowScan). Their wavelengths are calibrated with a wavemeter (HighFinesse WS6-600) to an accuracy better than the laser linewidth ( $< 0.05$  cm<sup>-1</sup>). The visible laser beams intersect the molecular beam perpendicularly between the

extraction plates of the time-of-flight mass spectrometer. The IR beam from the FHI-FEL is loosely focussed counterpropagating the molecular beam. For the spectroscopy of ground-state DyO, the FEL macropulse (about 10  $\mu$ s duration) ends 5  $\mu$ s before probing the population in the X8( $v = 1$ ) state, while for excitation of the  $n(J)$  Rydberg states the FEL pulse starts 0.5  $\mu$ s after their preparation. In these experiments, typical energies of the IR macropulse are a few tens of mJ in an approximately 5 mm diameter beam. Characterisation of the spectral profile of the FEL macropulse is done using an in-vacuum Czerny–Turner grating spectrometer (Acton VM-504, 75 lines per mm) combined with a pyroelectric linear array detector with 128 elements and a total width of 1/2 inch (DIAS Infrared 128LT).<sup>21</sup> By coupling a fraction of the light emitted from the IR-FEL into the spectrometer this allows for a shot-to-shot recording of its spectrum.

When first set up, the combination of grating spectrometer and array detector has been calibrated using a He–Ne laser, operating the grating in 2nd to 20th order. In the present study, the goal was to map the spectrum of the IR-FEL using well-known molecular transitions to obtain an independent and more accurate frequency calibration. For this one has to keep in mind that the pulse structure of the FEL, which contains micropulses of an (adjustable) duration between several 100 fs to a few ps, results in a comparably large Fourier transform-limited spectral bandwidth. The lowest achievable bandwidth in the mid-IR (around 1000 cm<sup>-1</sup>) is on the order of 2 cm<sup>-1</sup> (FWHM). In addition, inherent instabilities of the FEL's electron acceleration system result in a jittering around the central frequency which further broadens the spectral profile. The rovibrational spectrum of a reference molecule must therefore have large spacings between the rotational lines to be able to clearly resolve the spectral profile of the IR-FEL pulses. A large splitting can be realised in molecules with a large rotational constant,  $B$ , and/or by selectively studying transitions between levels with a high total angular momentum quantum number  $J$ . DyO is well suited for this purpose because the spacing between the two lowest rotational levels in the X8 state is already about 6.5 cm<sup>-1</sup>.<sup>9,10</sup> Moreover, the large value of  $\Omega$  ensures that the  $\Omega$ -doubling, *i.e.* the splitting between the opposite parity levels for each  $J$ , will be negligibly small. Furthermore, we can selectively record the IR transitions of the monoxide of the most abundant isotope <sup>164</sup>Dy with nuclear spin  $I = 0$ . The intrinsic spectral line-shape of IR transitions between rotational levels that can be considered fully degenerate parity doublets and that have no hyperfine structure basically is a delta-function. Given that for the  $v = 1 \leftarrow v = 0$  band in the X8 state of <sup>164</sup>DyO the absolute frequencies of the  $\Delta J = 0, \pm 1$  transitions are known to better than 0.005 cm<sup>-1</sup>, these transitions are ideally suited for our purpose.

## Results and discussion

### IR excitation in ground state neutral DyO

In earlier works, Cheng and Linton<sup>9,10</sup> have characterised the optical spectra of <sup>164</sup>DyO with high accuracy. Particularly relevant for the study here is that they determined  $\Delta G_{1/2}$  as well as



the rotational constants of  $\nu = 0$  and  $\nu = 1$  in the X8 state, from which the frequencies for the rotational lines of the  $\nu = 1 \leftarrow \nu = 0$  band can be accurately determined. As all rotational levels are degenerate parity doublets, the requirement for a change of parity in an electric dipole transition is fulfilled for all possible  $\Delta J = 0, \pm 1$  lines. To characterise the FEL spectrum in the mid-IR, the lowest R-branch lines of the  $\nu = 1 \leftarrow \nu = 0$  band appear to be best suited as these are rather isolated and go from the highest populated  $J$  levels in  $\nu = 0$  to much less populated  $\nu = 1, J + 1$  levels. The frequency of the R(8) line is precisely known as  $848.108 \text{ cm}^{-1}$  while the R(9) line is at  $848.793 \text{ cm}^{-1}$ .

Experimental IR spectra of  $^{164}\text{DyO}$  that reflect the change in population of the three lowest rotational levels ( $J = 8-10$ ) in the X8,  $\nu = 1$  state induced by IR excitation, are shown in Fig. 1. For this, the population in either one of these three rotational levels is probed *via* resonant excitation to rotational levels in the electronically excited  $[17.1]7$  state.<sup>9</sup> After a short delay of about 20 ns, the electronically excited molecules are ionised using the fourth harmonic of a Nd:YAG laser (266 nm), and the ions are mass-selectively detected. A two-color  $(1 + 1')$ -REMPI spectrum in the relevant spectral range is shown in the lower part of Fig. 2, in which the P(8), P(9), and P(10) lines that have been used for rotationally selective detection are marked with an asterisk. The P-lines are stronger than the Q-lines, which are again stronger than the R-lines in this electronic spectrum, as expected for a  $\Delta\Omega = -1$  transition. In the corresponding  $(1 + 1')$ -REMPI spectrum from the X8,  $\nu = 0$  state, shown in the upper part of Fig. 2, the P-lines are saturation broadened, and from their intensities, the Q- and R-lines are seen to be saturated as well. Note that the spectrum from the X8( $\nu = 1$ ) state has been up-shifted by  $841.7 \text{ cm}^{-1}$  to allow for a direct comparison between both spectra and for a rapid assignment of the rotational lines.

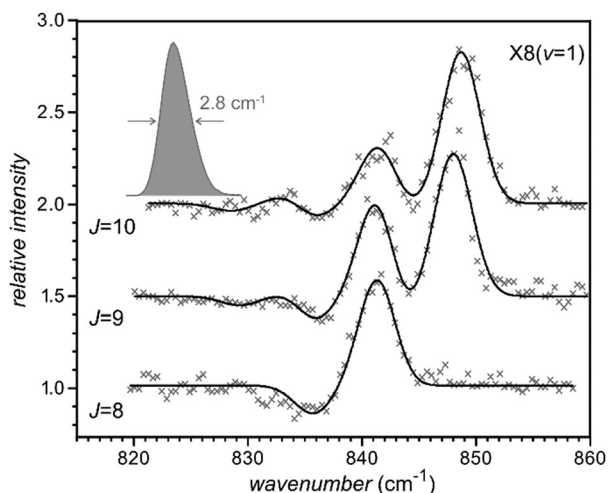


Fig. 1 IR spectra of  $^{164}\text{DyO}$  obtained by monitoring the change of population in three different rotational levels of X8( $\nu = 1$ ) upon IR excitation. The fits (solid lines) take both  $\nu = 1 \leftarrow \nu = 0$  (growth) and  $\nu = 2 \leftarrow \nu = 1$  (depletion) transitions into account. A typical time-averaged spectral profile of the IR radiation as recorded by the spectrometer is plotted in gray. The traces are shifted vertically and plotted on a common y-scale.

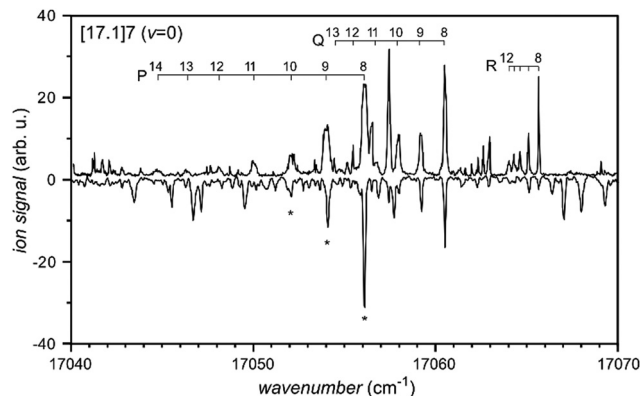


Fig. 2 Two-color  $(1 + 1')$ -REMPI spectra of the  $[17.1]7(\nu = 0) \leftarrow \text{X8}$  transitions for  $^{164}\text{DyO}$ . The frequency axis is for the upper spectrum, that starts from X8,  $\nu = 0$ . The lower spectrum starts from X8,  $\nu = 1$  and is up-shifted by  $841.7 \text{ cm}^{-1}$  to show the transitions on the same x-axis. Asterisks mark the three lowest lines of the P-branch that have been used to probe the population in X8,  $\nu = 1$  for the measurements in Fig. 1.

The middle and upper IR spectrum in Fig. 1, in which the  $J = 9$  and  $J = 10$  levels in X8,  $\nu = 1$  are probed, show the R(8) and R(9) lines, respectively, as the strongest and rather isolated lines. As there is hardly any overlap on their lower frequency sides with the Q-lines, the shape of both of these lines directly reflects the spectral shape of the IR-FEL. It is seen to compare well to the spectral shape as measured by the grating spectrometer, shown in the inset of Fig. 1. To match the centre frequencies of the R(8) and R(9) lines as determined by the spectrometer with the experimentally known frequencies, the spectrometer reading had to be adjusted by  $+0.8 \text{ cm}^{-1}$ . Even though the required adjustment is only a fraction of the bandwidth of the IR-FEL radiation, this more accurate calibration is significant.

Closer inspection of the spectra in Fig. 1 reveals that in addition to contributions from  $\nu = 1 \leftarrow \nu = 0$ , which increase the population in the probed levels, also transitions to the next higher vibrational level,  $\nu = 2 \leftarrow \nu = 1$ , are seen that decrease the population. These opposing contributions have an overall shift relative to each other given by twice the vibrational anharmonicity, *i.e.* by  $2\omega_e\chi_e$ , and will have slightly different spacings due to the slightly different rotational constants in  $\nu = 0$  and  $\nu = 2$ . Both contributions consist of only two rotational lines when probing  $J = 8$ , and it appears that the P(9) and Q(8) lines of the  $\nu = 1 \leftarrow \nu = 0$  band largely coincide with the Q(8) and R(8) lines of the  $\nu = 2 \leftarrow \nu = 1$  band, respectively. From this, it is concluded that  $2\omega_e\chi_e$  is about equal to the spacing between the two lowest rotational levels in X8, *i.e.* about  $6 \text{ cm}^{-1}$ . For a more detailed analysis, the energy of the  $(\nu, J)$  levels in the X8 ground-state are calculated from the parameters given in Table 1 *via*:

$$E(\nu, J) = T_v + B_v[J(J + 1) - \Omega^2]$$

where

$$T_v = T_0 + \omega_e\nu - \omega_e\chi_e\nu(\nu + 1) \text{ and } B_v = B_0 - \alpha\nu$$

**Table 1** Molecular constants of the X8 ground state of  $^{164}\text{Dy}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

X8	$T_v$	$B_v$
$v = 0$	0	0.358538(54) <sup>a</sup>
$v = 1$	841.6958(21) <sup>a</sup>	0.356943(12) <sup>a</sup>
$v = 2$	1677.6(2) <sup>b</sup>	0.35535 <sup>c</sup>

<sup>a</sup> Ref. 10. <sup>b</sup> This work. <sup>c</sup> Extrapolated from  $B_1$  and  $B_2$ .

Note that in defining it in this way,  $T_1 - T_0 = \omega_e - 2\omega_e x_e$ , commonly referred to as  $\Delta G_{1/2}$ . Table 1 lists the known values for  $T_0$  and  $T_1$  as well as for  $B_0$  and  $B_1$ , from which  $B_2$  has been linearly extrapolated.

The only free parameters for fitting the IR spectra are the value of  $T_2$  and the widths and intensities of the lines; the correction to the frequency axis of the grating spectrometer of  $+0.8 \text{ cm}^{-1}$  has already been applied in Fig. 1. The spectral lines are assumed to be Gaussian and to all have the same width. The best fit is obtained when a width (FWHM) of  $3.3 \text{ cm}^{-1}$  is assumed, about 20% larger than the width determined with the spectrometer, indicative of a slight saturation of the transitions.

From these fits a  $T_2$  value of  $1677.6(2) \text{ cm}^{-1}$  is obtained which results, together with the known value of  $T_1$ , in a vibrational constant of  $\omega_e = 847.5(2) \text{ cm}^{-1}$  and a vibrational anharmonicity parameter of  $\omega_e x_e = 2.9(1) \text{ cm}^{-1}$  for  $^{164}\text{DyO}$ . The uncertainty in the value of  $\omega_e x_e$  is mainly related to the ambiguity in locating the weak  $v = 2 \leftarrow v = 1$  signals. As an example, the decomposition of the IR spectrum obtained when monitoring the population in  $J = 10$  of X8,  $v = 1$  into the six Gaussian peaks is shown in Fig. 3.

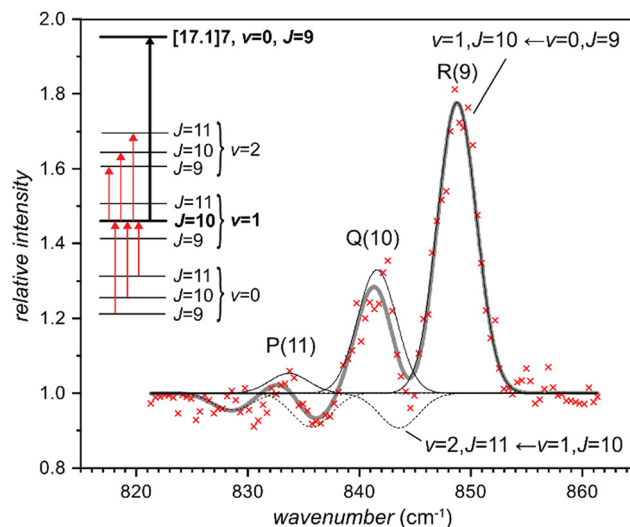
In earlier gas-phase measurements only the transition frequency for  $v = 1 \leftarrow v = 0$  ( $\Delta G_{1/2}$ ) had been determined. From this and the assumed dissociation limit of  $6.29 \text{ eV}^{24}$  estimates for  $\omega_e$  and  $\omega_e x_e$  of  $849 \text{ cm}^{-1}$  and  $3.5 \text{ cm}^{-1}$  have been reported.<sup>25</sup> These values agree well with the values experimentally determined here. Using density functional theory calculations with the B3LYP functional a vibrational constant of  $769 \text{ cm}^{-1}$  was predicted,<sup>26</sup> considerably lower than the experimental gas-phase value.

The relative intensities of the lines in the spectra shown in Fig. 1 can be qualitatively understood based on an estimated factor three reduction in the population with each increase of the vibrational quantum number and based on an approximate factor two reduction in the population with each higher rotational quantum number; the latter can be seen from Fig. 2. The Hönl-London factors ( $S^A$ ) for the P, Q, and R-lines are given by:<sup>27,28</sup>

$$S_{J''}^P = \frac{(J'' + \Omega)(J'' - \Omega)}{J''}$$

$$S_{J''}^Q = \frac{(2J'' + 1)\Omega^2}{J''(J'' + 1)}$$

$$S_{J''}^R = \frac{(J'' + 1 + \Omega)(J'' + 1 - \Omega)}{J'' + 1}$$



**Fig. 3** Fitted composition of the IR spectrum of  $^{164}\text{DyO}$  obtained when monitoring the population in  $J = 10$  of X8,  $v = 1$ . The experimentally observed IR transitions are indicated in the level scheme (red arrows) together with the P(10) probing transition. The fitted spectrum consists of lines belonging to the  $v = 1 \leftarrow v = 0$  band (solid) and to the  $v = 2 \leftarrow v = 1$  band (dashed). The sum of both (thick grey) reproduces the experimentally observed change in population upon IR excitation (red crosses) very well.

adding up to the degeneracy  $(2J'' + 1)$  of the starting level  $J''$ . Based on these Hönl-London factors and the abovementioned ratio of the vibrational and rotational populations in the X8 state, one would expect the Q-lines to be by far the strongest in the spectra shown in Fig. 1. In these experiments, the transitions are saturated, however, making the R-lines the strongest while the Hönl-London factors are less important. Assuming complete saturation of the transitions and an overlap of the P(9) and Q(8) lines of the  $v = 1 \leftarrow v = 0$  band with the Q(8) and R(8) lines of the  $v = 2 \leftarrow v = 1$  band, respectively, the observed fractional increase of the population around  $841 \text{ cm}^{-1}$  and the observed fractional decrease around  $835 \text{ cm}^{-1}$  in the lower spectrum of Fig. 1 can be well understood.

### IR-PIRI spectroscopy of $\text{DyO}^+$

Using the revised calibration of the FHI-FEL, IR spectra of gas-phase cationic  $\text{DyO}^+$  have been measured. These experiments rely on the general idea that core-nonpenetrating Rydberg states of the neutral molecule, *i.e.*, Rydberg states with a high value of the principal quantum number  $n$  and with an orbital angular momentum  $l \geq 2$ , may be understood as a cationic molecular core with an only weakly interacting electron on a large orbit. This Rydberg electron can be seen as spectator, and the molecule in the Rydberg state is similar to a weakly bound messenger complex.<sup>29</sup> Photoexcitation of the cationic core such that the total energy in the molecule is above its ionisation energy will lead to autoionisation.<sup>30</sup> An IR excitation spectrum measured *via* autoionisation of high- $n$  molecular Rydberg states thus provides vibrational data on the cationic core.<sup>31</sup> This experimental measurement method has been termed infrared photoinduced Rydberg ionisation (IR-PIRI)<sup>32</sup> and its





basic concept has been supported by a number of previous studies where, for instance, the influence of the principal quantum number  $n$  on the IR-PIRI spectra has been studied. In short, over a wide range of  $n = 7\text{--}93$  no detectable influence on band positions in IR-PIRI spectra has been found.<sup>33,34</sup> It should be noted, however, that these studies were for rather large molecules like *trans*-2-butene, *cis*-dichloroethene, or trichloro-ethene and that the thus obtained IR spectra had a rather limited resolution, possibly related to unresolved rotational band structures. While the band positions have been found to be independent of  $n$ , relative intensities of IR bands may be well affected as the spectral intensities in IR-PIRI depend not only on the IR absorption cross-sections but also on the decay dynamics of the different Rydberg states.<sup>34,35</sup>

For the IR-PIRI studies, DyO molecules have been prepared in different Rydberg states. Details of the two-color laser excitation scheme that is used to selectively prepare the  $^{161}\text{Dy}^{16}\text{O}$  isotopologue in specific  $n(J)$  levels are given elsewhere.<sup>20</sup> In the excitation region, a constant electric field of  $5\text{ V cm}^{-1}$  is applied. About  $1\text{ }\mu\text{s}$  after laser preparation of the Rydberg states an electric field is applied for ion-extraction. Three isolated Rydberg states  $n(J)$ , namely  $34(7.5)$ ,  $34(8.5)$ , and  $44(7.5)$ , have been used for these experiments. In  $34(7.5)$  and  $34(8.5)$ , the Rydberg electron is bound by about  $95\text{ cm}^{-1}$ , in  $44(7.5)$  by about  $57\text{ cm}^{-1}$ . The electric field used for ion-extraction is kept sufficiently low that none of these states will be field-ionised. Ions are only produced when the molecules in the Rydberg states interact with the IR radiation of the FHI-FEL. This interaction starts shortly after laser preparation of the Rydberg states, and lasts until the ions have been extracted, *i.e.* for less than a  $\mu\text{s}$ . The IR radiation produces prompt ions as well as highly excited neutral molecules that are subsequently field-ionised. The constant, weak electric field separates the prompt ions from the neutrals. After field-ionisation and ion-extraction the prompt ions and the delayed ions are separately detected. The IR-PIRI signal will appear in the prompt ion signal, as autoionisation is expected to be fast upon excitation of the ion core. As the highly excited neutral molecules can autoionise before the extraction field is applied, these can also partly contribute to the prompt ion signal.

In Fig. 4 the difference of the signal of the prompt ions and the delayed ions is plotted as a function of the IR excitation frequency in the  $880\text{--}930\text{ cm}^{-1}$  range. The signal of the delayed ions is subtracted after being multiplied with a factor that depends linearly on the IR frequency, such as to create a flat baseline in the resulting difference spectrum. This procedure is rationalised by the assumption that the autoionisation rate of the highly excited neutral molecules is a smooth function of the excitation energy. We have studied the effect of IR excitation in a much wider range of  $770\text{--}1000\text{ cm}^{-1}$  but only around  $910\text{ cm}^{-1}$  excess prompt ion signal has been reproducibly observed.

The IR-PIRI spectra obtained when starting from the Rydberg states  $34(7.5)$  and  $44(7.5)$  show a strong Q(7.5) line and a weaker but clearly discernible R(7.5) line. When starting from the  $34(8.5)$  state, the P(8.5) line can be recognised below the (not so well resolved) Q(8.5) and R(8.5) lines. The observed

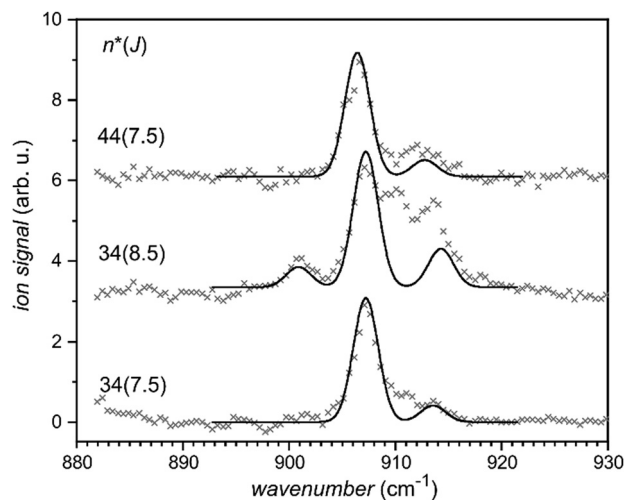


Fig. 4 IR-PIRI spectra of  $^{161}\text{DyO}$  in Rydberg states  $n(J)$ , *i.e.* with principal quantum number  $n$  and converging to the rotational level with total angular momentum  $J$  in the cation. The solid curves are fits of the rotational structure, taking a rotational constant of  $0.377\text{ cm}^{-1}$  for  $v = 1$  of the cation and relative line intensities governed by the Hönl–London factors. Gaussian lineshapes with a width (FWHM) of  $2.8\text{ cm}^{-1}$  are assumed. The traces are shifted vertically and plotted on a common y-scale.

spectra have been simulated using Gaussian lineshapes with a width (FWHM) of  $2.8\text{ cm}^{-1}$ . A rotational constant of  $0.377\text{ cm}^{-1}$  is taken, about 0.5% less than the measured rotational constant for  $v = 0$  of the cation, see ref. 20. The relative intensities of the P, Q and R lines are obtained from the expressions for the Hönl–London factors given earlier, and are seen to agree rather well with the experimental observations. As we are using less than  $1\text{ }\mu\text{s}$  of the  $10\text{ }\mu\text{s}$  duration macropulse of the FHI-FEL in these experiments, these transitions appear not to be saturated. The values obtained for  $\Delta G_{1/2}$  in the cation are not precisely identical and for  $34(7.5)$ ,  $34(8.5)$ , and  $44(7.5)$  values of  $907.4(2)\text{ cm}^{-1}$ ,  $907.4(4)\text{ cm}^{-1}$ , and  $906.6(2)\text{ cm}^{-1}$  have been found, respectively. While the first two values agree very well, the value found when starting from  $n = 44$  is slightly lower, even though the difference is still only a fraction of the bandwidth of the IR-FEL. This difference might be caused by the Stark-shift of the Rydberg levels in the weak electric field, which will be most prominent for the highest  $n$ , or due to a perturbation, just as it has been seen for Rydberg states of CO, for instance.<sup>36</sup> We therefore take a somewhat more conservative value for the overall uncertainty and determine the transition frequency as  $907 \pm 1\text{ cm}^{-1}$ .

### Comparison of lanthanoid monoxides, LnO and LnO<sup>+</sup>

The experimental value for  $\Delta G_{1/2}$  of the  $^{161}\text{DyO}^+$  cation of  $907(1)\text{ cm}^{-1}$  that we have found, fits well into the general trend for cationic lanthanoid monoxides. Existing theoretical predictions scatter that much, that a reasonable assignment based on those appears difficult. From DFT calculations vibrational frequencies in the range of  $936\text{--}983\text{ cm}^{-1}$  have been reported for the cationic ground state, depending on exchange–correlation functional and basis sets,<sup>12,26</sup> all well above the experimental value. On the other hand, potentially more accurate coupled cluster calculations (CCSD(T,25)) using a frozen core



predict a significantly lower value of  $873\text{ cm}^{-1}$ .<sup>12</sup> This value appears to be unrealistically small, because it is even less than the experimental value found in a Ne matrix. Different types of relativistic calculations predict an harmonic  $\omega_e$  in the rather wide range between  $843$  and  $1086\text{ cm}^{-1}$ , while Morse fits to the calculated potential curves give  $841\text{ cm}^{-1}$  for CASCI/CASSCF and  $873\text{ cm}^{-1}$  for X2C-CASSCF with an anharmonicity  $\omega_e x_e$  of  $7\text{ cm}^{-1}$ .<sup>19</sup>

A comparison of vibrational frequencies for lanthanoid monoxides and their cations is given in Table 2 and Fig. 5 and contains the values measured *via* matrix isolation IR spectroscopy<sup>13,14,37,38</sup> in cryogenic Ar and Ne matrices as well as gas-phase data. Values for gas-phase species have been obtained *via* a number of different techniques, *i.e.*, emission,<sup>39–41</sup> (spectrally dispersed) laser induced fluorescence,<sup>42–48</sup> mass analysed threshold ionisation (MATI),<sup>4,5</sup> (anion) photoelectron<sup>3,49,50</sup> spectroscopies or IR dissociation spectroscopy of He messenger complexes.<sup>51</sup> When available, also the vibrational anharmonicity is included in the table.

Overall, the stretching frequencies of both,  $\text{LnO}$  and  $\text{LnO}^+$ , are slightly increasing with atomic number, but show pronounced minima for Eu and Yb, as discussed below. Values for  $\nu(\text{LnO})$  in a cryogenic Ar matrix have been determined for all lanthanoid monoxides, while in the less interacting Ne matrix only about half of the lanthanoids have been studied.<sup>13–15,38</sup> Due to the interaction with the matrices,  $\nu(\text{LnO})$  values determined in Ar and Ne are significantly lowered compared to those found in the gas phase. These shifts are on average  $15\text{ cm}^{-1}$  ( $4\text{ cm}^{-1}$  for Ne) in case of the neutral monoxides and  $\sim 40\text{ cm}^{-1}$  ( $10\text{--}20\text{ cm}^{-1}$  for Ne) for the cations.

The monoxides of Eu and Yb show significantly lower  $\nu(\text{LnO})$  in the neutral and cation, related to their configuration of the metal dication being  $4f^7 6s^0$  and  $4f^{14} 6s^0$ , while the other lanthanoids have a  $4f^{n-1} 6s^1$  configuration of the dication. The  $6s$  electron forms a non-bonding  $\sigma$  orbital in  $\text{LnO}$  and upon

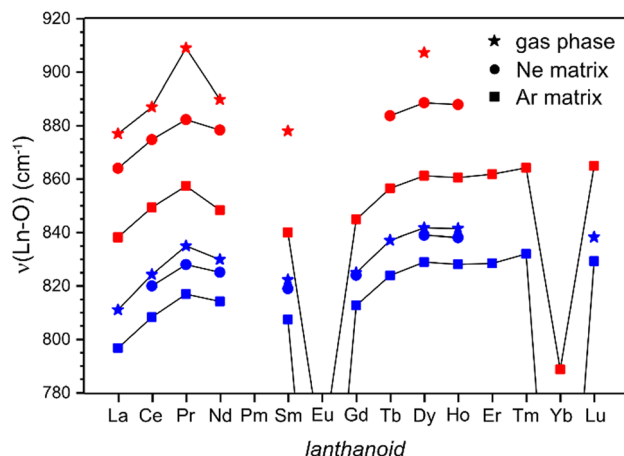


Fig. 5 Comparison of experimental values of  $\nu(\text{LnO})$  for cationic (red) and neutral (blue) lanthanoid monoxides obtained *via* IR spectroscopy in cryogenic Ar and Ne matrices, as well as in the gas phase ( $\Delta G_{1/2}$  values). There are no data for radioactive Pm.

ionisation it is removed for all Ln except for Eu and Yb leading to an increase of  $\nu(\text{LnO}^+)$  compared to  $\nu(\text{LnO})$ . On the other hand, removal of a  $4f$  electron (ionisation of  $\text{EuO}$  and  $\text{YbO}$ ) leads to a larger increase of  $\nu(\text{LnO}^+)$  as it affects the shielding of the metal core stronger and, hence, results in a stronger Coulomb interaction between the metal and  $\text{O}^{2-}$ . In the same vein, the  $4f^7$  and  $4f^{14}$  configurations in  $\text{EuO}$  and  $\text{YbO}$  effectively screen the metal core leading to a significantly reduced force constant also in the neutral species compared to other  $\text{LnO}$ .<sup>16</sup>

## Conclusions

Vibrational spectroscopic information has been obtained for gas-phase  $\text{DyO}$  and  $\text{DyO}^+$  using an infrared free electron laser.

**Table 2** Vibrational frequencies of  $\text{LnO}$  and  $\text{LnO}^+$  in cryogenic Ar and Ne matrices as well as gas-phase values for  $\omega_e$  and  $\omega_e x_e$  (in  $\text{cm}^{-1}$ ). The matrix IR data are averaged values for the isotopic distributions. Values for the vibrational transition frequency,  $\Delta G_{1/2,\text{gas}}$ , have either been measured directly or calculated from the reported vibrational constants and anharmonicity parameters. If values are given for a specific isotopologue, this is usually for the most abundant one

	$\nu(\text{LnO})$ matrix				$\nu(\text{LnO}^+)$ matrix						Ref.
	Ar	Ne	$\Delta G_{1/2,\text{gas}}$		Ar	Ne	$\Delta G_{1/2,\text{gas}}$				
La	796.7		811.07	817.26	3.097	838.2	864.0 <sup>a</sup>	877 <sup>e</sup>			4, 37 and 39
Ce	808.3	820	824.3	827.7	1.7	849.4	874.8 <sup>a</sup>	887 <sup>e</sup>			4, 13, 38 and 42
Pr	816.9	828.0	835 <sup>b</sup>			857.4	882.3	909 <sup>b</sup>			5, 13 and 38
Nd	814.2	825.1	829.9	834.1	2.1	848.3	878.4	889.8	892.4	1.3	3, 13, 38, 43 and 49
Pm	—	—	—	—	—	—	—	—	—	—	
Sm	807.4	819	822.32			840.0		878 <sup>c</sup>			13
Eu	667.8					756.9					38
Gd	812.7	824	824.99	829.25	2.13	844.8					13, 38 and 40
Tb	823.9		837.1			856.5	883.7 <sup>a</sup>				13, 14 and 45
Dy	829.0	839.0	841.69	847.5 <sup>d</sup>	2.9 <sup>d</sup>	861.2	888.6	907 <sup>f</sup>			13 and 14
Ho	828.1	838.1	841.4			860.5	887.9				13, 14 and 46
Er	828.5					861.8					13 and 14
Tm	832.0					864.2					13 and 14
Yb	660.0		683.1			788.7					14 and 47
Lu	829.3		838.3	844.5	3.1	864.9					13, 14 and 41

<sup>a</sup> Unpublished, see ref. 15. <sup>b</sup> MATI, uncertainty  $\pm 5\text{ cm}^{-1}$ . <sup>c</sup> IR-PD of  $\text{SmO}^+\text{He}_n$  ( $n = 1\text{--}3$ ) complexes, extrapolated from observed shifts of  $\sim 2\text{ cm}^{-1}/\text{He}$ . <sup>d</sup> This work, value for  $^{164}\text{DyO}$ . <sup>e</sup> MATI. <sup>f</sup> This work, for  $^{161}\text{DyO}$ , uncertainty  $\pm 1\text{ cm}^{-1}$ .



Due to the large value of the total angular momentum in the ground state of both species, rotationally resolved IR spectra could be measured. For neutral DyO the vibrational constant and the vibrational anharmonicity have been determined as  $\omega_e = 847.5(2) \text{ cm}^{-1}$  and  $\omega_e x_e = 2.9(1) \text{ cm}^{-1}$ , which agree with previous estimates. For the cation the vibrational transition frequency  $\Delta G_{1/2}$  has been obtained as  $907(1) \text{ cm}^{-1}$ , which is the first gas-phase value for  $\nu(\text{DyO}^+)$ . The assignment for  $\nu(\text{DyO}^+)$  relies on the assumption that the IR-PIRI scheme probes an essentially undisturbed cationic core. The latter is substantiated by the observation of P, Q and R lines in the IR-PIRI spectra with relative intensities just as expected for a  $\nu = 1 \leftarrow \nu = 0$  transition in the ion.

The various excitation and detection schemes applied here are rather unusual in the spectroscopy of diatomic molecules for which vibrational data is frequently extracted from rotationally and vibrationally resolved electronic spectra. Similar experiments to ours, using an IR free electron laser but without resolving any rotational structures in the IR spectra, have been performed before only for CO.<sup>52</sup> The combination of IR excitation with rotationally state-selective ionisation detection schemes as shown here provides an alternative way to obtain vibrational data for systems with complex electronic spectra.

## Author contributions

Sascha Schaller: investigation (equal); data curation (lead); writing – original draft (supporting); writing – review and editing (equal). Sandy Gewinner: investigation (supporting); writing – review and editing (equal). Wieland Schöllkopf: investigation (supporting); writing – review and editing (equal). Gerard Meijer: supervision (lead); conceptualization (equal); writing – review and editing (lead). André Fielicke: conceptualization (equal); investigation (equal); writing – original draft (lead); writing – review and editing (equal).

## Data availability

The spectroscopic data supporting this article is included in the figures of the article.

## Conflicts of interest

There are no conflicts to declare.

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