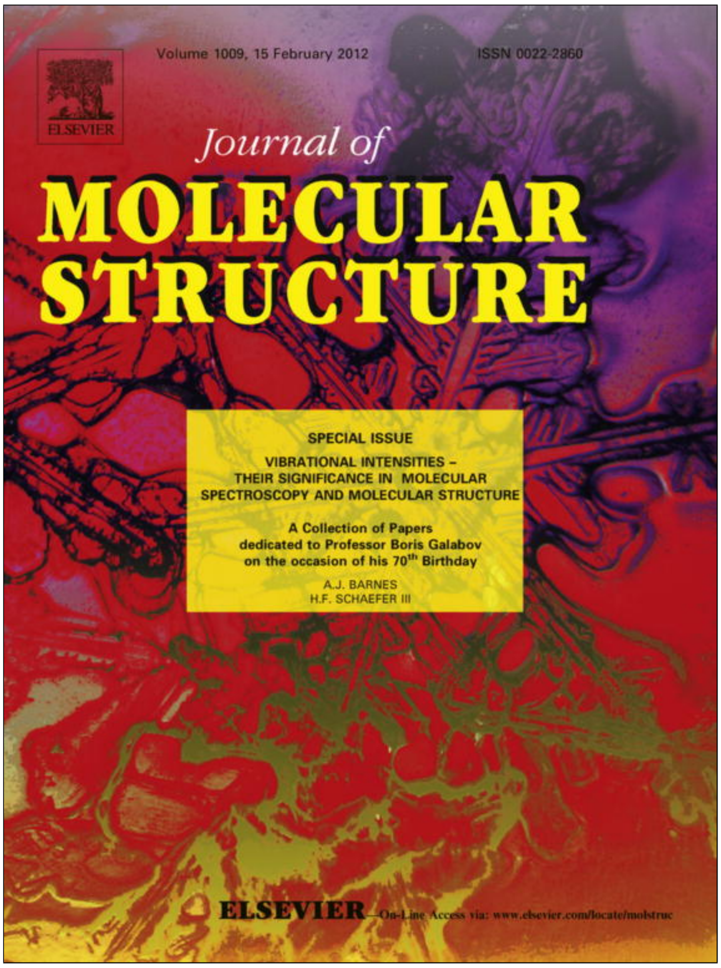

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SPECTROSCOPY AND MOLECULAR STRUCTURE

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The role of intensities in determining characteristics of spectroscopic networks ☆

Tibor Furtenbacher, Attila G. Császár *

Laboratory of Molecular Spectroscopy, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

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ABSTRACT

Spectroscopic networks (SNs) are large, finite, weighted, undirected, rooted graphs, where the vertices are discrete energy levels, the edges are transitions, and the weights are transition intensities. While first-principles SNs are "deterministic" by definition, if a realistic transition intensity cut-off is employed during the construction of these SNs, a certain randomness ("stochasticity") is introduced. Experiments naturally build random graphs. It is shown on the example of the $HD^{16}O$ isotopologue of the water molecule how intensities, in the present case one-photon absorption intensities, determine the structure as well as the degree distribution and edge density of SNs. The degree distribution of realistic computed SNs can be described as scale free, with the usual and well known consequences. Experimental SNs, based on measured and assigned transitions, also turn out to be scale free. The graph-theoretical view of high-resolution molecular spectra offers several new ideas for improving the accuracy and robustness of information systems containing spectroscopic data. For example, it is shown that most all rotational–vibrational energy levels are involved in at least a few relatively strong transitions suggesting that an almost complete coverage of experimental quality energy levels can be deduced from measurements.

1. Introduction

In recent publications [1–5] we introduced the notion of spectroscopic networks (SNs) in order to characterize molecular spectra measured under high resolution. The principal reason to introduce a network-theoretical view of molecular spectra observed under high resolution was that SNs were expected to prove to be useful for improving the accuracy and completeness of existing experimental spectroscopic information systems and the accuracy of theoretical line lists [1–16], containing the essence of molecular spectra and thus transforming data into knowledge.

For individual molecules, quantum mechanics results in energy levels and selection rules which in turn can be used to build large, finite, deterministic, undirected, weighted, rooted networks [graphs, $G = (V, E, W)$], made up of energy levels as nodes (vertices, V) and allowed transitions between them as links (edges, E), while weights (W) are related to transition intensities. Different spectroscopic techniques are characterized by different transitions and transition intensities and thus different links and weights. Experiments, via high-resolution techniques of molecular spectroscopy, lead to a subgraph of complete SNs (see, *e.g.*, Fig. 1). Even in the experimentally most thoroughly studied cases the observable transitions form just a tiny part of all the transitions allowed [3,4]. The complete and accurate line list information about allowed transitions related to a given experiment, corresponding to an extremely large SN, can only be determined *via* sophisticated, variational-type quantum chemical computations; see, for example, Refs. [17–22]. In the present work, only networks corresponding to one-photon absorption spectra are investigated. Note that single-photon absorption experiments provide most of the data collected in spectroscopic information systems.

There are several questions one might ask about SNs (see Section 2 for a detailed description of the graph-theoretical terms used here). First, one is interested in the degree, *i.e.*, size–frequency, distribution of SNs. Erdős–Rényi random networks [23,24], (left panel of Fig. 2) exhibit a characteristic mean value for the probability $P(d)$ characterizing nodes having degree d. In this case a large number of nodes have an about average number of connections and increasingly less and less have a higher or lower number of links. For most complex networks [25–31] the size–frequency distribution of the links shows what is referred to as scale-free behavior. Scale-free random networks (right panel of Fig. 2) are characterized by a simple power-law degree distribution corresponding to rare frequent events and common rare ones. Second, one may wonder how many components experimental and computed SNs have and what the edge density of the components is. Third, it is important to know whether experimental and computed first-principles SNs have the same degree distribution or not. Related to this is the question whether computed SNs change their degree distribution when intensity cut-offs are employed, as done in this study, to

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☆ This paper is dedicated to Prof. Boris Galabov, an esteemed colleague and co-author of the widely read book "Vibrational intensities" (Elsevier, Amsterdam, 1996), on the occasion of his 70th birthday.

* Corresponding author. Tel.: +36 1 372 2929; fax: +36 1 372 2592.
E-mail address: csaszar@chem.elte.hu (A.G. Császár).

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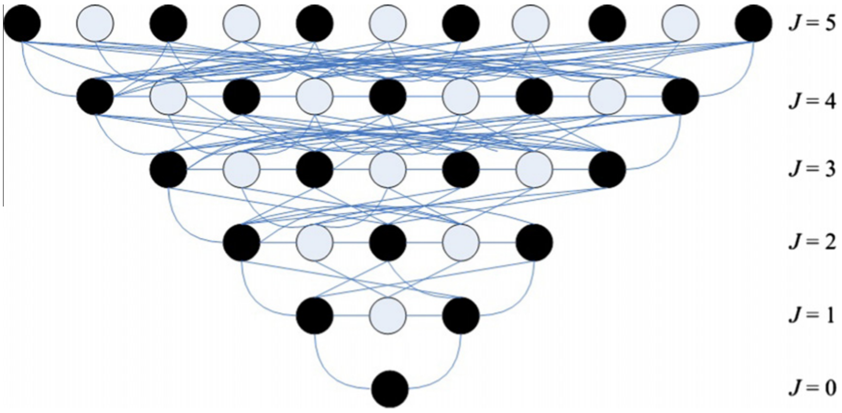

Fig. 1. The complete purely rotational one-photon absorption spectroscopic network (SN) of the HD^{16}O isotopologue of water for its ground vibrational state (the single root of the graph is the $J_{K_aK_c} = 0_{00}$ state), up to $J = 5$, where J is the quantum number describing the overall rotation of the molecule. Missing from the figure are the weights of the links associated with absorption intensities. Filled and empty nodes correspond to even and odd rotational parities, respectively, defined by $(-1)^{J+K_c}$, where K_c is an asymmetric-top quantum number (see text).

determine the size of the computed subgraph. Fourth, one would like to answer whether SNs are stochastic or deterministic and under what conditions would there be a transition between the two. Note that complete computed SNs, containing all possible energy levels and all allowed transitions, are clearly fully deterministic. Fifth, one would like to know whether most energy levels are involved, at least occasionally, in relatively strong transitions allowing their experimental determination or whether the majority of energy levels are involved only in weak transitions whose knowledge may be unimportant from a practical point of view. In other words, one would like to know the minimal number of transitions needed to determine all the energy levels of a molecule through readily available experimental techniques. Sixth, error and attack tolerance [27] of SNs tells us important details about the connectivity and robustness of SNs. Finally, the all-important question is whether a graph-theoretical view of molecular spectroscopy could offer any new insights and significant consequences during experimental or computational investigations of high-resolution molecular spectra.

The molecule HD^{16}O, hereafter called HDO, was chosen for this investigation as it was the subject of a large number of experimental high-resolution spectroscopic studies validated recently [4] via a robust inversion algorithm called MARVEL [2] (MARVEL stands for Measured Active Rotational–Vibrational Energy Levels), a first-principles line list, including energy levels, transitions, and one-photon absorption intensities, is available for it [21], and the first-principles SN consists of a single component as all of the nuclei of HDO are different. The experimental dataset of Ref. [4] contains 8819 nodes and 54,740 links (of which 36,690 are unique), forming a multiedge graph. The computed network of HDO employed here contains altogether 163,491 nodes and 697,444,828 links forming a simple graph (see Table 1). The latter numbers exemplify the complexity of SNs. It must also be added that the line list employed [21] contains energy levels computed only up to 25,000 cm^{-1} (the D_0 dissociation energy of water isotopologues is on the order of 41,000 cm^{-1}) and the J values, where J is the quantum number characterizing overall rotation, terminate at $J = 50$ (the coverage is not complete). Selected characteristics of the first-principles SNs employed in this study are provided in Table 1.

2. Elements of network (graph) theory

For the purposes of the present discussion, networks and graphs [32] are considered to be equivalent mathematical constructs. The two most important families of random graphs of particular concern here are Erdős–Rényi [24] and scale-free (Barabási) [25,33] graphs (see Fig. 2 for simple examples). Random and scale-free networks have drastically different characteristics. Before reviewing these, we give a few useful definitions of graph theory relevant for spectroscopic networks.

Intuitively, a graph is a representation of a set of objects where certain pairs of the objects are connected by links. Mathematically, a *graph* G is an ordered pair, $G = (V, E)$, where V is a set of *vertices* and E is a set of *edges*, the edges being 2-element subsets of V. If $V' \subseteq V$ and $E' \subseteq E$, then $G' = (V', E')$ is a *subgraph* of $G = (V, E)$. Energy levels and transitions represented in a graph G corresponding to an SN form V and E, respectively. An SN of a molecule can be denoted as G^{mol}, in our case $G^{\mathrm{HDO}} = (V^{\mathrm{HDO}}, E^{\mathrm{HDO}})$. Further parameters characterizing an SN (G), *e.g.*, temperature, measurement characteristics, and intensity cut-off value, can be listed as subscripts. The number of edges that connect to a vertex is called the *degree* of the vertex. As true for all graphs, the sum of the vertex degrees is twice the number of edges. Each edge $e = \{u, v\} \in E$ connects two adjacent vertices u, $v \in V$. If $u = v$, the edge is called a *loop*. SNs do not contain loops but they are often *multiedge* graphs containing multiple edges (between the same pair of vertices), corresponding to multiple measurements of a certain transition. Graphs which contain neither loops nor multiple edges are called *simple graphs*. First-principles SNs corresponding to arbitrary measurement techniques are simple graphs. If the edges have no direction the graph is also called *undirected*, otherwise it is called *directed*. Spectroscopic networks dealt with here are undirected graphs. A *path* P of *length* k, denoted as P^k, is a non-empty graph $P = (V, E)$ of the form $V = \{x_0, x_1, \ldots, x_k\}$ and $E = \{x_0x_1, x_1x_2, \ldots, x_{k-1}x_k\}$, where the x_i are all distinct. A graph G is called *connected* if there is a path between any pair of its vertices. Otherwise it is called *disconnected*. A connected subgraph of G is called a *component* of G. First-principles SNs are undirected, simple, connected graphs. A *rooted graph* contains distinguished vertices. SNs contain two types of components, rooted and other. SNs can have more than one root. A *cycle* exists in a graph if there is a path starting from v_1 and returning to v_1 along at least three edges. SNs contain a large number of cycles of widely differing size. Connected graphs without cycles are called *trees*. Arbitrary, connected or disconnected, graphs without cycles are called *forests*. Sometimes it is useful to assign *weights* to the vertices or edges of the graph. In SNs non-negative transition intensities are assigned to edges as weights.

For undirected simple graphs the *edge density* is defined as $D = 2|E|/[|V|(|V| - 1)]$, where $|V|$ and $|E|$ are the number of vertices and edges of the graph, respectively. While in simple graphs the

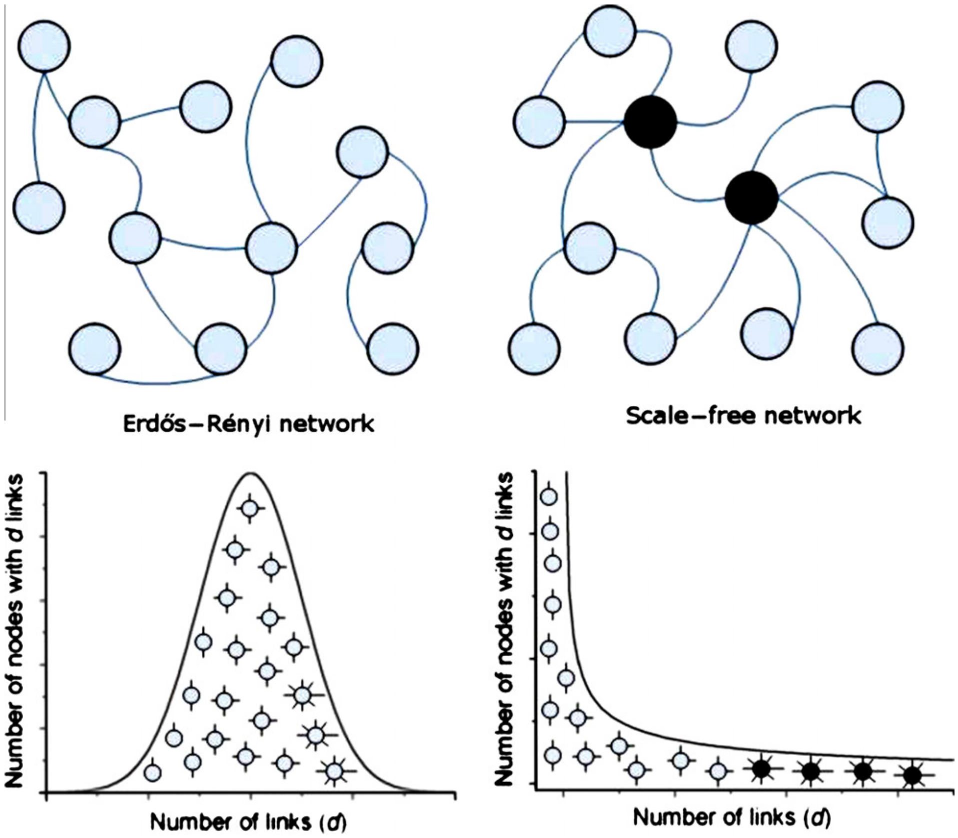

Fig. 2. Pictorial representations and degree distributions of random networks of Erdős–Rényi and of scale-free character, the so-called hubs (nodes with a large number of links) are shown in black in the latter case.

Table 1
Selected characteristics of first-principles one-photon absorption spectroscopic networks (graphs) of HDO, based on subgraphs of the complete graph corresponding to the line list of Ref. [21] and obtained after selecting only those links (edges) which have an intensity larger than the "intensity cut-off" value given.

Intensity cut-off[a]	No. of vertices, $\lvert V\rvert$	No. of edges, $\lvert E\rvert$	Edge density, D[b]	Maximum degree
10^{-20}	329	836	0.015494	20
10^{-22}	1427	5623	0.005527	79
10^{-24}	3891	23,120	0.003055	205
10^{-26}	9915	76,108	0.001548	488
10^{-28}	23,312	231,714	0.000853	1196
10^{-30}	62,139	738,870	0.000383	4042
10^{-40}	157,174	24,377,001	0.001974	11,680
10^{-50}	162,924	143,681,730	0.010826	11,705
10^{-60}	163,491	399,516,009	0.029894	11,705
10^{-70}	163,491	655,091,117	0.049016	11,705
10^{-80}	163,491	697,404,016	0.052183	11,705
10^{-90}	163,491	697,444,828	0.052186	11,705

[a] Intensity given in cm molecule^{-1}.

[b] $D = 2\lvert E\rvert/[\lvert V\rvert(\lvert V\rvert - 1)]$, where $\lvert V\rvert$ and $\lvert E\rvert$ are the number of vertices and edges of the graph, respectively.

maximum number of edges is $\lvert V\rvert(\lvert V\rvert - 1)/2$, in SNs this is much smaller due to the existence of quantum mechanical selection rules.

Erdős–Rényi random graphs are built by considering a process whereby links are added randomly to vertices. Erdős–Rényi graphs with a fixed set of V_{fix} vertices have a "characteristic" degree $2E/V_{\mathrm{fix}}$, *i.e.*, the vertex degrees have approximately a Poisson distribution with a mean of $2E/V_{\mathrm{fix}}$ (see Fig. 2). If a random graph is allowed to grow and links are added by preferential attachment, *i.e.*, based on probabilities proportional to the momentary degree of the vertices, a *scale-free random graph* results [34]. The scale-free property of a network means that the probability that a randomly selected node has exactly d links is $P(d) \propto d^{-\gamma}$, where γ is called the *scaling index* [31]. Scale-free random networks, as opposed to Erdős–Rényi random networks, are characterized by (a) a relatively few nodes with a large number of links (these nodes are called *hubs*) and (b) a robust connectivity structure hard to fragment by random removal of nodes. The following dynamical features are the usually assumed requirements of a scale-free random network: (a) evolutionary growth with more or less random generation of new nodes, (b) highly interactive self-organization, and (c) preferential connectivity of new nodes to old ones. Hubs create short paths between vertices of the graph.

Many networks can be characterized by a small *diameter* [33,34]. The diameter of a network corresponds to the average length of the shortest paths defined by the links connecting any two nodes of the network. It has been recognized a long time ago [35] that some graphs with a large number of vertices v have a diameter around log v or even log v/loglog v. This property of networks is referred to as *small-world phenomenon*.

3. Degree distribution of first-principles SNs

Linear-scale size–frequency [$d - P(d)$] plots for first-principles one-photon absorption transitions for HDO are shown in Fig. 3, based on a recent computed line list [21]. Very clearly, for all experimentally relevant intensity cut-offs, down to 10^{-30} cm molecule^{-1}, the plots corresponding to a sequence of simple graphs show high similarity. As the intensity cut-off takes smaller values, the largest d value, as expected, increases, while, at the same time, max[$P(d)$] decreases. Due to the fact that at cut-off values smaller than about 10^{-30} cm molecule^{-1} the line list is incomplete, the corresponding plots are not shown.

Log–log plots of the $d - P(d)$ distributions are often used to reveal scale-free behavior of networks. Apart from the very low and very high d parts, the panels of Fig. 4 indicate a power-law behavior over several orders of magnitude with a scaling index, γ, of about 0.9, close to 1. This value is quite different from the usually obtained γ = 2–3 values for large, complex, scale-free networks [31]. This suggests a less rapid decrease of the distribution function of SNs, revealing that most nodes of an SN naturally have a small number of transitions. The graphs with an intensity cut-off larger than about 10^{-30} cm molecule^{-1} are clear indicators of the scale-free property of SNs.

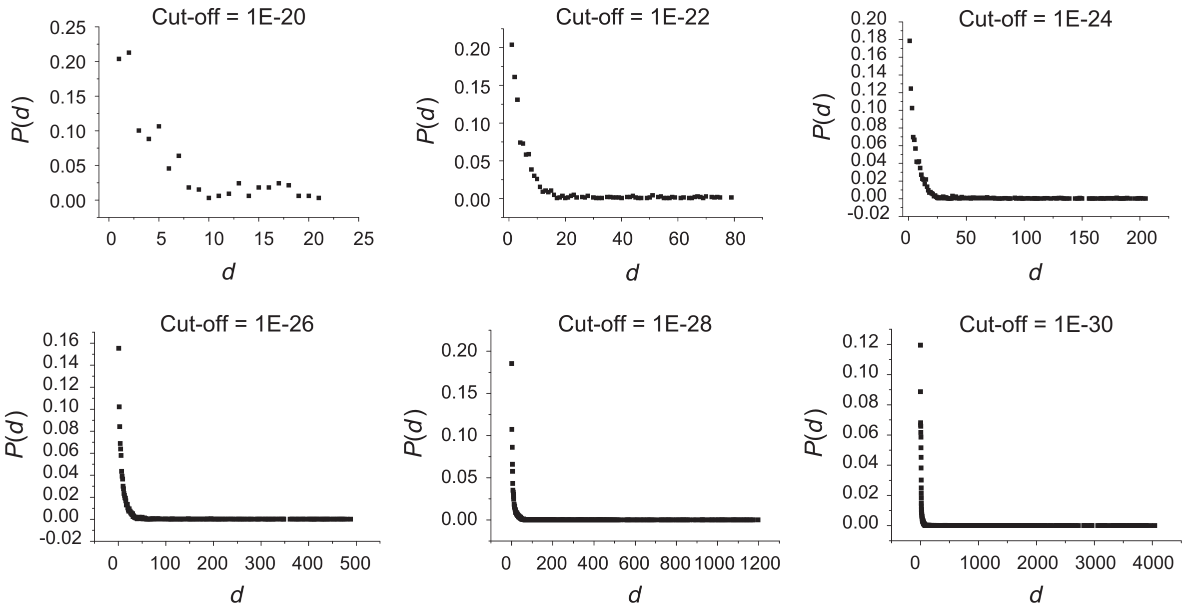

Fig. 3. Distribution of links among nodes given as linear scale size–frequency [$d - P(d)$] plots, where $P(d)$ is the proportion of vertices with degree d, for first-principles one-photon absorption transitions for HDO, based on the line list of Ref. [21] and using various intensity cut-off values between 10^{-20} and 10^{-30} cm molecule^{-1}.

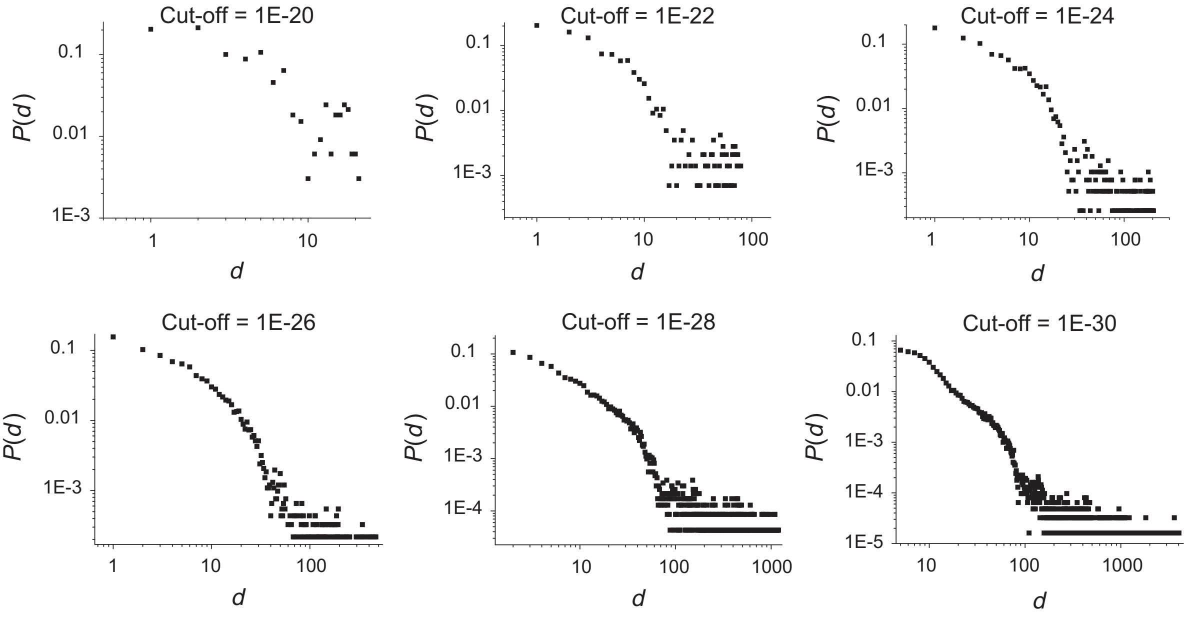

Fig. 4. Log–log size–frequency [$d - P(d)$] plots for first-principles one-photon absorption transitions for HDO, with various absorption intensity cut-off values between 10^{-20} and 10^{-30} cm molecule^{-1}.

4. First-principles vs. experimental degree distributions in SNs

Given the scale-free behavior of first-principles SNs with "realistic" intensity cut-offs, it is particularly interesting to investigate how SNs built upon experimentally measured transitions behave as far as the degree distribution is considered. As Fig. 5 demonstrates, the experimental SN of HDO [4] shows a clear scale-free behavior. This is quite expected as the experimental SN was built by a quasi-random addition of new nodes and links and it is also reasonable to expect that preferential attachment governs the growth of the network.

5. Number of components of SNs

SNs of molecules may have components as required by nuclear spin statistics [36]. For example, symmetric isotopologues of water (*e.g.*, $H_2{}^{17}O$ or $H_2{}^{18}O$) have two components, traditionally called ortho and para [depending on whether the spins of the protons are parallel (ortho, total nuclear spin $I = 1$) or antiparallel (para, $I = 0$)]. Under field-free conditions, transitions are not allowed between the two components [37]. HDO, with all of its nuclei different, has only a single theoretical component, *i.e.*, all of its energy levels form part of a simple connected graph. Additional selection rules may put constraints on the changes of the "good" and approximate quantum numbers, describing the energy levels involved in the transitions.

Fig. 1 shows the lowest-energy part of the complete purely rotational one-photon absorption SN of HDO, without the weights and up to $J = 5$, where J is the rotational quantum number [38]. The connectivity is defined here by well-known selection rules of quantum mechanics for one-photon absorption spectroscopy. Selection rules state for HDO that if $\Delta J = 0(\pm1)$ than $p = \pm1(0)$, where p is the parity describing the energy level. These selection rules dictate that if $J - K_c$, called rotational parity, is even or odd then the maximum number of pure rotational transitions from a given rovibrational energy level with asymmetric-top label [38] $J_{K_aK_c}$ is $3J + 2$ or $3J + 1$, respectively, as shown in Fig. 1. Note that measurements miss several purely rotational transitions even for low J values even in the case of this thoroughly studied isotopologue of water. As J increases, the number of transitions not measured increases quickly. Note also that while many of the transitions are not directly measured, their identification in experimental spectra becomes straightforward if inverted rovibrational energies obtained, for example, via the MARVEL protocol [2] are available and the transition intensity is high enough [39].

Components of experimental SNs arise due to other reasons, as well. First, experimental SNs form multiedge graphs and perhaps never are simple graphs. Second, as measurements show some randomness, spectroscopic measurements often result in several components. Previously [2], we named these disconnected components of the SN floating spectroscopic networks (FSNs) or orphans (if the component contains only two vertices). We have not found cases where first-principles SNs contained, at whatever intensity cut-off value, disconnected components.

6. Hubs and edge densities

Scale-free networks contain a few hubs, *i.e.*, nodes with relatively large number of connections. As expected, the most important hubs in a one-photon absorption SN are on the ground vibrational state. For the measured SN of G^{HDO} they are as follows: $J_{K_aK_c} = 4_{22}$, 4_{23}, and 3_{13}, with 605, 583, and 565 links, respectively. In the computed SN, with a cut-off value of 10^{-30} cm molecule^{-1}, the nodes with the largest number of connections are 6_{34}(4042), 7_{35}(3970), and 6_{24}(3897), where the number of links is given in parentheses.

The edge density D of the first-principles SN has a minimum (Table 1). This minimum is achieved at an intensity value which is about the limit for present-day absorption measurements. Nevertheless, it must not be forgotten that the investigated line list becomes incomplete at about this cut-off value.

The interconnectedness of a particular spectroscopic network can be described efficiently by a single number, the diameter [34]. The diameter computed statistically for the measured SN of HDO is only about 7, though it is still considerably larger than the corresponding log v value, about 3. This value is slightly larger but similar to the diameter of the first-principles SN. As the absorption intensity cut-off is decreased, the diameter of the computed SN seems to stay around this value though becomes smaller. Thus, SNs clearly have an intrinsic small-world property, similarly to most other complex networks studied in nature, society, communication, and elsewhere [40].

7. Stochasticity of SNs

Complex scale-free networks have usually been studied via principally *stochastic* models [31]. Note in this respect that first-principles SNs are principally deterministic and stochasticity is introduced, whether experimentally or in computations, via "realistic" intensity cut-offs. Thus, SNs offer an interesting class of networks for future studies also from this respect.

8. Number of nodes vs. number of links

The size of a first-principles SN, both in the number of nodes and links, depends heavily on the chosen cut-off of the one-photon absorption and emission intensities, which are both a function of

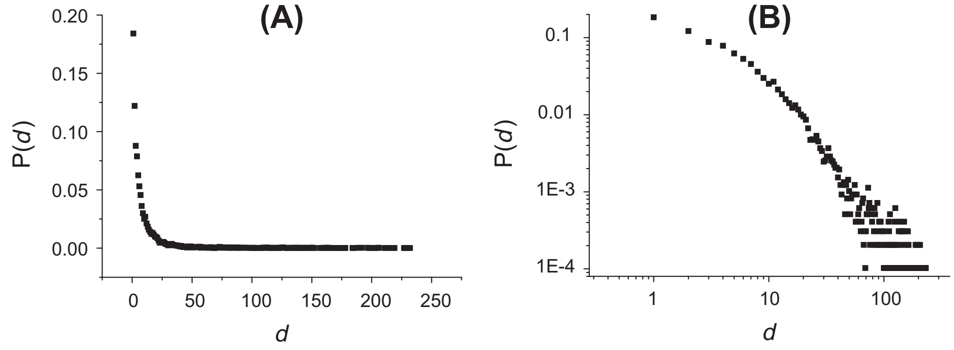

Fig. 5. Size–frequency [$d - P(d)$] (Panel A) and log–log size–frequency (Panel B) plots for experimental one-photon absorption transitions for HDO.

the temperature. All the results reported here for the computed one-photon absorption SN correspond to a temperature of 300 K.

From the numbers in Table 1 and Fig. 6 one can conclude that it is easy to find a few relatively strong transitions for almost all nodes in the SN but the great majority of the transitions is extremely weak. Nevertheless, these characteristics of first-principles SNs suggests that with relatively standard measurements almost all of the energy levels can be determined which in turn could lead to an almost complete knowledge of experimental absorption spectra if transitions based on "measured" energy levels were augmented with computed line intensity values.

9. Error and attack tolerance of SNs

Selection rules allow only a limited number of links between the nodes of the SN. As the spectroscopic network becomes larger, either via new measurements or by a decrease in the intensity cut-off value, the number of links increases substantially but not the number of nodes (see Fig. 6). The number of cycles within the network also increases drastically. This ensures that SNs have an extremely robust structure.

Robustness of the SN can be investigated the following way. Let us remove nodes one by one from the original SN having nodes M in a completely random way and determine size N of the largest component. After random removal of nodes the relative size of the largest remaining network compared to the full size of the remaining network stays very close to 1 even if up to 70% of the nodes are removed (see Fig. 7). The network is only destroyed when about 85% of the nodes are randomly removed. This extreme error tolerance is another characteristic property of SNs.

A particularly important conclusion for MARVEL-type [2] analyses of measured spectra appears to be the fact that it is "allowed" to delete some of the measured transitions, most likely those with large uncertainties, as this should not lead to a deletion of a large number of energy levels and a collapse of the SN.

10. Usefulness of the graph-theoretical view of high-resolution spectroscopy

Interpretation of the results of high-resolution spectroscopic experiments via graph theory offers distinct new ideas and algorithms to improve the accuracy, completeness, and robustness of line lists. Having complete and accurate line lists for molecules of, for example, atmospheric and astrophysical interest at arbitrary temperatures is one of the "holy grails" of modern high-resolution spectroscopy. While at present experimental line lists are accurate and incomplete, theoretical ones are less accurate but more complete.

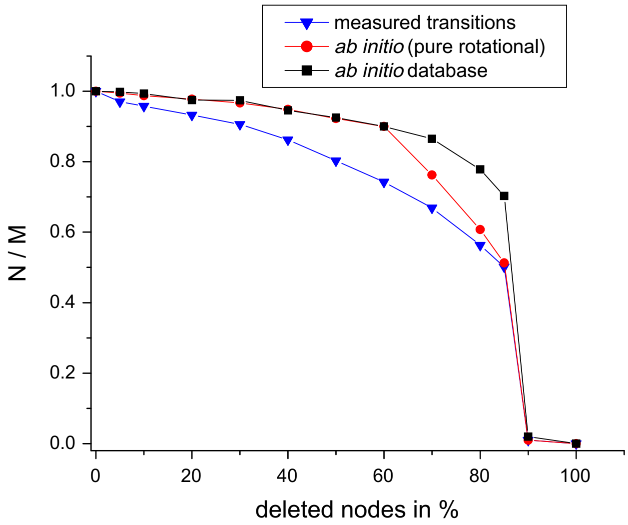

Fig. 7. Fragmentation dynamics of spectroscopic networks following random removal of nodes, where N/M means the number of nodes within the largest remaining network (N) compared to the maximum number of nodes (M) in the SN.

The scale-free property of SNs described means that despite the fact that SNs can be extremely large, though always finite in realistic cases, there are only relatively few energy levels whose accuracy determines principally the accuracy of the experimental SN. Consequently, experiments which improve the accuracy of SNs by decreasing the uncertainties of energy levels qualifying to be hubs are the most useful ones. This leads to the important conclusion that all microwave, millimeterwave, and far-infrared measurements performed with this aim in mind would be highly beneficial for improving the overall accuracy of experimental SNs of molecules of prime interest. Note that the distinguished role of long-wavelength measurements has traditionally been exploited when using combination differences for understanding spectra.

Unification of graph components is important for several reasons. First, it allows the attachment of proper energy values to the vertices of disjoint components. Second, it helps to improve the robustness of the SN. Third, it may lead to the design of new experiments to improve the SN. Investigation of the minimum weight spanning forest should tell us how to connect FSNs and orphans to components containing one of the roots of the SN in the most simple and efficient way. Note that since each link has a unique weight (unique intensity), there will be a unique minimum weight spanning tree for each component. Though this may not result in the most viable experiment it should certainly help designing it.

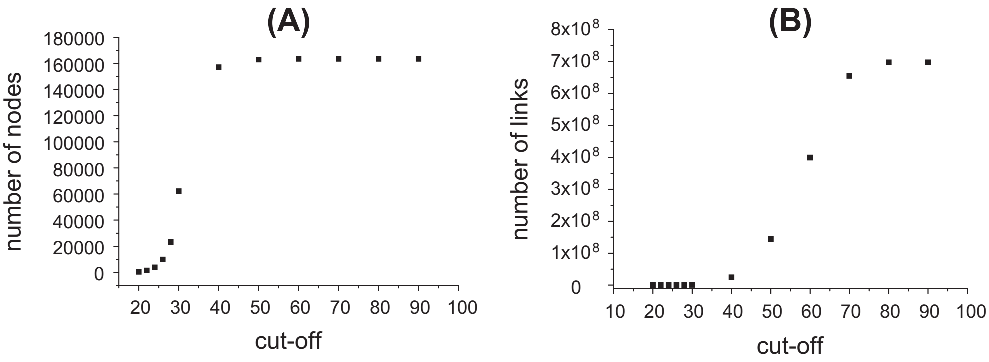

Fig. 6. The number of nodes (Panel A) and links (Panel B) as a function of the negative logarithm of the computed 300 K one-photon absorption intensities ("cut-off"), based on the line list of Ref. [21].

Thorough comparison of the experimental and the computed SNs results in the identification of the least well determined hubs present in the experimental SN. This is another useful bit of information about the SN. For example, as shown in Fig. 4 of Ref. [5], detailed comparison of measured and computed hubs helps to determine the "weakest nodes" within the experimental SN and to design new experiments which help, with a minimum amount of effort, the determination of a more accurate and more robust SN.

11. Summary and conclusions

We suggested before that in order to make maximum use of experimental spectroscopic line list information, by now available for a relatively large number of molecules including their isotopologues, they should be viewed as weighted, undirected, and rooted graphs, which we call spectroscopic networks (SNs). The vertices of the graphs are the energy levels, the edges are the spectroscopically allowed transitions, and the weights are the transition intensities. It is clear that intensities have a crucial role in determining the structure of SNs. Of course, different spectroscopic techniques yield SNs with drastically different topologies.

Experiments yield relatively small multiedge random graphs. First-principles computations result in very large deterministic simple graphs. As demonstrated in this study for the case of the one-photon absorption spectrum of HDO, many of the popular notions of interdisciplinary scientific, social, and communication network investigations, like scale-free and "small world" properties, hubs, network dynamics, self-organization, robustness, and attack/error tolerance, are all relevant when characterizing SNs.

The network-theoretical view of high-resolution molecular spectra advocated here offers several advantages toward the complete characterization of spectra. The scale-free property of the overall network degree distribution established leads to the useful concept of hubs, *i.e.*, nodes with a large number of links. This in turn provides design ideas for new spectroscopic measurements. For example, measuring the least well characterized hubs of the SN leads straightforwardly to a more accurate and more robust SN.

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